

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



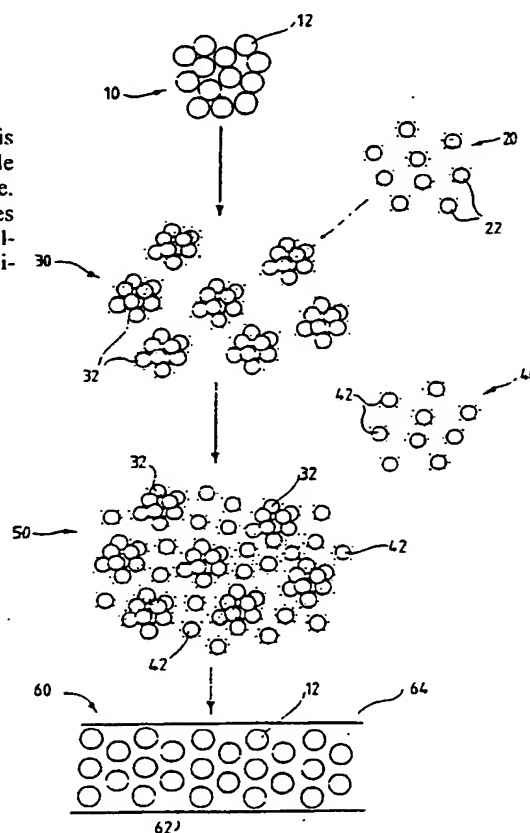
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>5</sup> : C09D 5/02, 7/12, 7/00 C09C 1/00		A1	(11) International Publication Number: <b>WO 93/12184</b>
			(43) International Publication Date: 24 June 1993 (24.06.93)
(21) International Application Number: PCT/US92/09731		(74) Agents: SLUZAS, Alex, R. et al.; Paul & Paul, 2900 Two Thousand Market Street, Philadelphia, PA 19103 (US).	
(22) International Filing Date: 12 November 1992 (12.11.92)			
(30) Priority data: 801,974 3 December 1991 (03.12.91) US 801,975 3 December 1991 (03.12.91) US 801,992 3 December 1991 (03.12.91) US		(81) Designated States: AT, AU, BB, BG, BR, CA, CH, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MW, NL, NO, PL, RO, RU, SD, SE, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG).	
(60) Parent Application or Grant (63) Related by Continuation US Filed on 07/801,974 (CIP) 3 December 1991 (03.12.91)		Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(71) Applicant (for all designated States except US): ROHM AND HAAS COMPANY [US/US]; Independence Mall West, Philadelphia, PA 19105 (US).			
(72) Inventors; and (75) Inventors/Applicants (for US only): VOGEL, Martin [US/US]; 550 Pine Tree Road, Jenkintown, PA 19046 (US). KOSTANSEK, Edward, C. [US/US]; 2425 Durham Road, Buckingham, PA 18912 (US). THIBEAULT, Jack, C. [US/US]; 10-1 Aspen Way, Doylestown, PA 18901 (US). SPERRY, Peter, R. [US/US]; 49 Woodview Drive, Doylestown, PA 18901 (US). LINDER, Linus, W. [US/US]; 1624 Clearview Road, Lansdale, PA 19446 (US). CHUNG, Chao-Jen [US/US]; 1220 Turnbury Lane, North Wales, PA 19454 (US). EMMONS, William, D. [US/US]; 1411 Holcombe Road, Huntingdon Valley, PA 19006 (US).			

(54) Title: PROCESS FOR PARTICLE ADSORPTION

(57) Abstract

A process for forming a suspension of discrete composite particles is described. Each composite particle comprising an insoluble first particle and at least one insoluble second particle on the surface of the first particle. The process comprises mixing the first particles with the second particles under conditions to form a suspension free of agglomerate comprising multiple first particles and agglomerate consisting of just multiple second particles.



**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Côte d'Ivoire	LI	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	MC	Monaco	TG	Togo
DE	Germany	MD	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

### PROCESS FOR PARTICLE ADSORPTION

The present invention relates to a process for particle adsorption. In particular, the present invention relates to a process for preparing a composite particle wherein at least one second particle is adsorbed on the surface of a first particle. The present invention also relates to a suspension of the composite particles.

Generally, the present invention relates to a process for preparing aqueous compositions including inorganic material particles, such as  $\text{TiO}_2$  and/or clay particles. More particularly, the present invention relates to the dispersion and distribution of inorganic material particles in products formed by the loss of water from such aqueous compositions.

Aqueous dispersions of polymeric latex are used to prepare a tremendous variety of commercially important products, including paints, coatings, primers, mastics, caulks, binders for non-woven materials, and adhesives. Frequently, the polymeric latex is included to form a continuous phase as the water is lost in order to bind the product together, and to contribute important physical properties. In addition to the polymeric latex, most products include particles of one or more inorganic materials. Some inorganic materials contribute an important functional property to the product, such as fire resistance, sheen, flattening, hardness, color, texture, opacity, or toughness. Often these inorganic materials are relatively expensive, and it is desirable to employ them in the formulated product as efficiently as possible.

For example, titanium dioxide has been for many years the pigment of choice for conferring opacity to plastic sheets and films, and particularly to coatings formed from coating compositions and paints. In paints titanium dioxide is typically the most expensive component of the formulation on a volume basis. It has been an ongoing objective of the coatings industry to achieve the desired degree of opacity in a coating while at the same time using as little titanium dioxide pigment as possible. One way in which this is done is by

employing titanium dioxide which has an optimal average particle size and particle size distribution for scattering light. Another way of making efficient use of the titanium dioxide employed is by dispersing this pigment as well as possible.

Agglomerated or aggregated titanium dioxide pigment particles make less than their full potential contribution to the performance of the coatings, such as, for example, with regard to coating opacity and colorant potential. Such aggregates can also impair certain other properties of the coating or film such as, for example, strength and resistance properties. Titanium dioxide is often sold as a dry powder. As a practical matter, this powder must to be milled in a liquid medium to break up agglomerates and to obtain a colloidally stable dispersion.

In order to stabilize the coating formulation against settling or flocculation, a variety of surface active dispersing additives have been used. Coatings manufacturers have often used titanium dioxide as a dry powder, which is used directly in preparing coating compositions. In this case, a dispersing additive is usually added directly to the pigment and a small amount of water in a preliminary pigment "grind" step in which loose agglomerates of the pigment particles are broken up by mechanical shear forces. The dispersing additive typically remains in the mix through the subsequent steps in the coating preparation process and typically will be found in the fully formulated coating composition.

There has been an increasing tendency for titanium dioxide to be commercially supplied in concentrated slurry form, such as, for example, in water. However, since the titanium dioxide particles in the slurries are prone to aggregation upon storage, the slurries often need to be redispersed for maximum effectiveness before use in formulating a coating composition. Either the manufacturer of the titanium dioxide slurry or the end user of the slurry, and sometimes both, may perform the redispersion step. This step is another source of dispersing agent in the fully formulated coating.

The opacifying capability or hiding power of a paint or coating is a function of the spacing of the titanium pigment particles in the dried coating. The light scattering characteristics of titanium dioxide particles are well known. The



average size and size distribution of titanium dioxide particles used for opacifying purposes has been highly optimized by the titanium dioxide manufacturers for maximum scattering. Maximum light scattering occurs when the titanium dioxide pigment particles have a diameter of from about 200 to about 250 nanometers and are spaced far apart from each other, on the order of a few particle diameters, so that there is minimal interference between the light scattering of neighboring particles.

In practice, however, for example in the formulation of paints, it is widely recognized that when enough titanium dioxide particles have been dispersed into the polymeric coating vehicle to yield films of acceptable opacity, the level of opacity which is achieved is significantly less than would be theoretically predicted from the light scattering potential of a single titanium dioxide particle multiplied by the total number of particles in the path of light passing through the film.

A number of factors have been identified which partially account for the diminution of opacity from the theoretical predictions. If two or more titanium dioxide particles are in actual contact with each other, or even if they are closer together than the optimum spacing distance, the particles will behave like a single aggregated larger particle and result in reduced light scattering. This occurs if the titanium dioxide particles are not adequately deaggregated during the dispersion process. However, even if the titanium dioxide particles are fully deaggregated in the dispersion process, a random distribution of particles will not provide the maximum scattering achievable in theory if the particles were optimally distributed.

In a related phenomenon, referred to as "crowding", titanium dioxide pigment particles are forced to be nearer to each other than the desired optimum merely by the lack of available space. This lack of available space may be caused by the space taken up by the other coating fillers and extenders which are of a comparable size to, or which are larger than, the pigment particles. In the case of polymeric binders, which are particulate in nature prior to film formation, such as, for example, latex or emulsion polymers, and in the case of nonaqueous dispersion polymers, the binder polymer particles themselves can crowd

pigment particles, especially if they are of comparable or larger in size than the titanium dioxide particles.

In other instances, the inorganic materials, for example, fillers, may be less expensive than the latex and it may be desired to incorporate the maximum amounts possible without compromising the desirable properties attributable to the latex, such as, for example, binding and tensile properties, such as elongation and, in the case of adhesives, minimum loss of tackiness. Since the polymeric latex is typically the most expensive component of the formulated product, inexpensive inorganic materials are frequently included to reduce product cost. In this case, it is desirable to use the greatest possible volume of the inexpensive inorganic material, while still retaining the desired performance properties of the product, since these properties typically decline when too much of the inexpensive inorganic material is included. A good example is a paint formulated with so much of an inexpensive filler pigment, such as calcium carbonate, that the critical pigment volume concentration is exceeded. Such a paint will provide a much less protective coating for a surface on which it is applied than a similar paint formulated with slightly less filler, and having a pigment volume concentration below the critical level.

One way of making efficient use of the inorganic material employed is by dispersing this pigment as well as possible. Agglomerated or aggregated inorganic material pigment particles frequently make less than their full potential contribution to the performance of the product, such as, for example, strength and resistance properties. Inorganic materials are typically sold as dry powders. As a practical matter, this powder must be milled in a liquid medium to break up agglomerates and to obtain a colloidally stable dispersion.

In order to stabilize the product formulation against settling or flocculation, a variety of surface active dispersing additives have been used. Manufacturers have often used inorganic materials as dry powders. In this case, a dispersing additive is usually added directly to the material and a small amount of water in a preliminary "grind" step in which loose agglomerates of the inorganic material particles are broken up by mechanical shear forces. The dispersing additive typically remains in the mix through the subsequent steps in the product

preparation process and typically will be found in the fully formulated product composition.

Sometimes inorganic materials are commercially supplied in concentrated slurry form, such as, for example, in water. However, since the inorganic material particles in the slurries are prone to aggregation upon storage, the slurries often need to be redispersed for maximum effectiveness before use in formulating a coating composition. Either the manufacturer of the inorganic material slurry or the end user of the slurry, and sometimes both, may perform the redispersion step. This step is another source of dispersing agent in the fully formulated product.

The traditional guiding rule or goal in the formulation of practical, dispersed inorganic material-containing products, such as coatings, including for example, pigmented latex paints, is to make the inorganic material dispersion and the polymeric latex binder dispersions as colloidally stable and compatible with each other as possible, in the sense that they can be mixed without formation of coagulum or like aggregate or excessive increases in viscosity. It has heretofore been found that inorganic material particles cannot be effectively dispersed into aqueous latex compositions by simply blending or directly mixing them into the aqueous polymeric latex composition. When such direct blending of inorganic material particles has been attempted, agglomeration of the particles has resulted in the formation of grit or coagulum in the composition. Products containing grit or coagulum may suffer the loss of properties such as gloss, mechanical strength and impermeability. Even in the case of nonaqueous (solvent-borne) or 100% solids polymer compositions, high energy grinding or milling input has been found to be necessary to deagglomerate and wet out the inorganic material particles. Even with the use of such operations, inferior dispersions containing aggregates of inorganic material particles result unless significant quantities of dispersing, wetting or "coupling" agents are employed. However, even when such agents are used, the distribution of the inorganic material particles in the polymer system at best approaches that of a random distribution. As a result there exist a substantial number of particles in close proximity to each other, and possibly in direct physical contact with each other, especially in mastics, caulks,

and like materials.

In the case of many compositions including polymeric latex, such as polymeric latex adhesives, and latex paints and coatings, it is conventional practice to first form a stable aqueous dispersion of the inorganic materials including the pigments, fillers and extenders. This dispersion, also known as a "grind" or "millbase," may contain water-miscible solvents, such as for example glycols and glycol ethers, and relatively low molecular weight water soluble polyelectrolytes as inorganic material pigment grinding aids or dispersants. Generally, these pigment dispersants are anionic polyelectrolytes. Many different types of such dispersants are known. For example, U.S. Patent 2,930,775 discloses the water soluble salts of diisobutylene maleic anhydride copolymers having molecular weights between about 750 and 5,000 as dispersants when employed at concentrations of from about 0.05 to 4% on pigment weight. U.S. Patent 4,102,843 and U.S. Reissue Patent 31,936 disclose the use of water soluble salts of copolymers of hydroxyalkyl (meth)acrylates and (meth)acrylic acid of molecular weights of from 500 to 15,000 at concentrations of from about 0.01 to 5% on pigment to produce glossy emulsion paints. U.S. Patent 4,243,430 discloses a water-soluble dispersant comprising an addition copolymer comprising greater than 30% alpha, beta-unsaturated monovinylidene carboxylic acid, the copolymer having an apparent pKa between 6.0 and 7.5 and molecular weight between about 500 and 15,000, and forming a water soluble salt with zinc ammonia complex ion. Low molecular weight polyphosphate salts, such as potassium tripolyphosphate, are also used because they are relatively inexpensive, but they tend to have marginal hydrolytic stability.

The use of these and other polyelectrolyte dispersants is described in T.C. Patton, Paint Flow and Pigment Dispersion (Wiley Interscience, 2nd edition) 290-295 (1979). Also described therein (pages 468-497) are a number of milling devices used in the preparation of pigment dispersions. One such device which is commonly used in the manufacture of latex paints is the high speed disk disperser designed to develop high shearing forces in the pigment grinding step. Common practice is to use the device with dispersant to form a stable dispersion of inorganic material pigment, and then to add to the dispersion the aqueous

latex polymer binder along with the other ingredients, such as for example thickeners and rheology modifiers, antifoaming agents, colorants, coalescing agents or temporary plasticizers for the latex polymer particles, and surfactants for substrate wetting and colorant compatibility. The pigment dispersion process and the relation to flocculation and other properties are discussed further in Treatise on Coatings, Vol. III, Part 1 (Marcel Decker) (1975); Pigment Handbook, Vol. I (2nd edition, Wiley Interscience) (1988), and Pigment Handbook, Vol. III (Wiley Interscience) (1973). Other types of pigment dispersion equipment are also employed, including ball mills, sand mills, Banbury mixers, and the like, depending on the nature and physical characteristics of the product.

While these polymeric dispersants and procedures enable the formulation of practical aqueous formulations, they have certain undesirable characteristics. Because of their ionic nature, polyelectrolyte dispersants tend to impart water sensitivity to films, which can result in reduced resistance of the films to scrubbing, and increased swelling with a tendency towards delamination and blistering. Similarly, the presence of polyelectrolyte dispersants can reduce the corrosion resistance of coatings films applied to steel surfaces. Moreover, such polyelectrolyte stabilized dispersions of inorganic material particles are prone to flocculation and reaggregation by other ionic species in the aqueous formulation, such as, for example, from initiator residues and from soluble inorganic pigments, especially those which contribute multivalent ions such as zinc oxide and calcium carbonate. Furthermore, since films dry by water evaporation, the concentration of such ionic species in the coating or film increases upon drying, and an otherwise suitable dispersion may become aggregated during the drying process itself. The stability and instability of inorganic material dispersions in the presence of polyelectrolytes and multivalent metal ions has been described by Burlamacchi, et al., Colloids and Surfaces 7, 165 (1982).

Even in the unlikely case that a polyelectrolyte dispersant were to confer effective dispersion of inorganic material pigment particles to provide a dispersion of singlet particles, the range of distance of the repulsive forces between particles is very small, typically on the order of less than about 100 Angstroms (10 nanometers), in relation to the size of inorganic material

particles, which can range from on the order of 50 nanometers or so (such as for fumed silica) to several thousand nanometers (such as for coarse calcium carbonate). Consequently, the repulsive forces between particles in such dispersions would be incapable of maintaining any significant degree of spacing between the inorganic material particles to improve the scattering or hiding power in the case of the dispersed titanium dioxide pigment, or to have a significant impact on the mechanical properties of the dried film.

A number of techniques have been proposed to disperse inorganic particles such as inorganic material particles in aqueous polymer containing coating compositions.

For example, U.S. Patent 4,608,401 discloses a method for encapsulating solid particles by admixing the particles in an aqueous reaction medium with a water-insoluble polymerizable monomer in the presence of nonionic surface active stabilizing agent (such as a polyethoxylated alkylphenol containing at least about 8 carbon atoms in the alkyl group and preferably at least 40-50 ethylene oxide groups per molecule) to form a water-insoluble polymer free of ionic charge. A redox polymerization is employed which is free of ionic groups and does not release ionic groups in the reaction medium. The starting particles must be free of significant levels of ionic charge, either anionic or cationic, existing either from their structure or generated during their preparation and handling through electrolyte additions.

The '401 patent states that "[p]articles which are charged have been found not to participate in the present encapsulation mechanism but, in fact, to severely inhibit the same, resulting in virtually immediate flocculation of the entire solids" (column 7, line 62 - column 8, line 4).

Naturally agglomerated particulate materials are taught as being effectively dispersed in situ during the polymerization, eliminating the necessity for preliminary grinding and/or dispersion treatments. The '401 patent teaches that agglomerates of the inorganic pigment particles, which are present before and during the initiation of the polymerization reaction, are broken down or "exploded" apart during the polymerization. The behavior of the system has not been explained.

Latex paints prepared using pigment dispersed according to the procedure of the '401 patent are claimed to exhibit improved gloss, opacity, and scrub resistance relative to paints prepared by conventional means, although details for the preparation of the latter including the method of pigment dispersion and the characteristics of the latex polymer to be used, are not provided. The entire amount of polymer which appears in the final paints of the '401 patent is introduced in the polymerization process in the presence of the pigment. The process for achieving pigment encapsulation requires the handling of reactive monomers and other ancillary chemicals and the conducting of chemical reactions in the presence of pigment as an integral part of the process.

U.S. Patent 4,025,463 is directed towards stabilizing aqueous inorganic material pigment slurries by blending plastic pigment with the slurry. At least about 10% of nonfilm-forming polymer latexes of 1,000-10,000 Angstroms in size, and having a glass transition temperature greater than 30 C, are blended with about 10-50% water. The '483 patent discloses stabilizing such slurries against gravitational separation and sedimentation upon storage of the slurry. In the illustrative examples, Tamol 731 dispersant is used at a concentration of 0.35% on pigment. The '483 patent does not disclose or teach adsorption of the latex on the inorganic material particles. While the slurry containing latex in patent Example 1 has a total volume solids of about 41% compared to the control dispersion of Example 3 which has a total volume solids of about 31%, it is possible that increased volume solids alone might be expected to retard the rate of settling. While the systems which are compared are of approximately the same initial viscosity, the control system contains much more methyl cellulose thickener.

U.S. Patent 4,315,959 relates to a process for coating microscopic substrates, such as pigment particles, dispersed in an aqueous medium containing a complex of a polyhydroxylated polymer, preferably polyvinyl alcohol ("PVA"), and a transition metal, most preferably copper II. The complex forms a layer on the particles which initiates polymerization of monomers such as acrylates and methacrylates. Example 1 discloses polymethylmethacrylate coated on inorganic material on a first layer of the PVA/Cu II complex. Tests such as electron

microscopy and Hegman fineness show that the size of the treated particles was very nearly identical to the size of the untreated particles. Example 6 is directed to kaolin and talc coated with polymethyl methacrylate and show a higher modulus of elasticity relative to untreated materials in polymethyl methacrylate or using a known anchoring agent. As in the '401 patent, the process of achieving layering of a polymer on pigment involves conducting chemical reactions in the presence of the pigment. See also P. Godard et al., Double Liaison, No. 387-388, p.II (1988).

U.S. Patent 4,800,103 describes a process which involves treating a particulate inorganic material with the latex by mixing the latex with an aqueous suspension containing from 5-50% by weight of the inorganic material, adding a water-soluble salt having a multivalent cation, and adjusting the pH of the suspension to more than 4.0 in order to coagulate the latex-treated material to form an open three-dimensional network of larger flocs. The flocculated material is then dewatered and the resultant cake is dried and then pulverized. Alternatively, the latex may be added to a suspension of the inorganic material with a suitable dispersing agent for the inorganic material. The resultant mixture is then spray dried. An object of this invention is to prepare anhydrous compositions that may be easily incorporated in resins for castings, such as, for example, polyurethanes, unsaturated polyesters, acrylics, nylon and polypropylene.

U.S. Patent 4,421,660 discloses the steps of emulsifying a hydrophobic, emulsion polymerizable monomer in an aqueous colloidal dispersion of discrete particles of an inorganic solid, and subjecting the resulting emulsion to emulsion polymerization conditions to form a stable, fluid, aqueous colloidal dispersion of the inorganic solid particles dispersed in a matrix of water-insoluble polymer of the hydrophobic monomer. An aqueous dispersion of the inorganic material is first made using surfactants such as fatty acid salts, polysoaps such as sodium polyacrylate, and especially polysoaps such as potassium salts of functionalized oligomers, such as for example the Uniroyal Chemical Polywet varieties. In Example 6 inorganic material of 200-400 nanometers in diameter is polymerized with a styrene/butyl acrylate



composition to yield a bimodal dispersion of mean diameters of 650 nanometers and 110 nanometers. A coating, the composition of which is not described, prepared from the latex is reported as having excellent opacity. As in the prior references, the coating of the inorganic particles is achieved by an emulsion polymerization chemical reaction in the presence of the particles.

US-A-4,421,660 discloses a process for encapsulating inorganic particles by first emulsifying monomer in the presence of the particles and then polymerizing the monomer to yield multiple inorganic particles dispersed in a colloidal size polymer matrix.

US-A-4798854 discloses a process for forming under stable conditions dispersions of inorganic particles and polymeric particles and then coprecipitating the mixed suspension by adding a coagulant such as aluminium sulphate.

The attractive and repulsive forces which control the ability of particles of one type and size to adhere onto the surface of other particles have been the subject of extensive theoretical work and investigation with model systems, as evidenced by numerous publications. These publications typically refer to the phenomenon of particle-particle adhesion as "heterocoagulation", and discuss maximizing the freedom of dissimilar particles from undesirable heterocoagulation in very dilute systems. The theory of so called "heterocoagulation" processes has been described by an extension of the well-known colloidal stability theory of Derjaguin, Landau, Verwey and Overbeek ("DLVO theory"). This extension is given by the Hogg, Healy and Furstenaue equation which extended the DLVO theory to include the interaction between spherical colloidal particles of different radii, unequal surface potentials and differing London-van der Waals (i.e. Hamaker) constants, and is described in R. Buscall, et al., Polymer Colloids (Elsevier Applied Science Publications 1985) pages 89-90 and 165-167.

DLVO theory mathematically expresses a balance between attractive forces attributed to van der Waals forces and repulsive forces attributed to like electrical charges on the surfaces of interacting particles. Other types of interaction forces, for example steric repulsion and attraction due to dissolved polymer, can be incorporated into the basic theory at least semi-quantitatively. Investigators

have shown the applicability of the theory in very dilute systems. Their conclusions are typically expressed in terms of particle collisions and minimum repulsive energy barriers between particles sufficient to overcome the attractive forces. Below this energy barrier there are too many collisions of particles with energies exceeding this minimum repulsive energy barrier to prevent coagulation. The relationship between this energy barrier and coagulation is taught as depending on several particle and medium variables which include medium dielectric constant, medium ionic strength, particle size, particle surface charge which may be expressed in terms of zeta potential, and the material attraction or Hamaker constant for colloidal materials immersed in the particular medium. No single parameter is, therefore, by itself a predictor of coagulation or stability.

If colloidal dispersions of particles differing in sign of charge are mixed, the usual result is a gross flocculation or coagulation. This result may be a desirable consequence in some circumstances, such as, for example, in instances where it is desired to purify water containing suspended matter or to isolate a bulk solid material from its colloidal suspension. If, however, the dispersions of particles having different sign of charge are mixed together under conditions of low particle concentration, and where one of the particle types is smaller than the other and present in greater number, then gross coagulation may be avoided and the smaller particles may form a monolayer on the larger ones.

However, the particle concentrations required to cleanly effect such a process, without forming significant quantities of coagulum or grit, are so low as to render such a process commercially impractical, since large volumes of liquid dispersions would have to be handled.

The DLVO theory and extensions thereof have been useful as a guide for interpreting and correlating aspects relating to the stability of small particles and dilute colloidal dispersions. These theories has been useful despite their quantitative limitations, and the fact that all of the necessary parameters for implementation, such as, for example, the material attraction or Hamaker constants, are not always known, or are not known with sufficient accuracy for all the materials of possible interest. The primary deficiency of the DLVO theory

is that it is limited to the interactions of two isolated particles of the same type with each other in very dilute dispersions.

Despite extensive research relating to the theory of particle interaction and extensive work with model systems at low particle concentrations, as reflected by numerous publications in the field of colloidal stability and heterocoagulation, the utility of the DVLO and other theories as relating to the preparation of commercial dispersions containing high concentrations of inorganic particles has not been established.

There is a continuing need to improve the effective utilization of inorganic material in aqueous compositions and thereby to improve the performance properties of the compositions. In addition, there is a need for a method of minimizing the viscosity of inorganic material slurries, and to quickly prepare such slurries. Further, there is a need for a process to disperse inorganic material particles at high concentrations for use in coating and related types of compositions with a minimal amount of dispersing surfactant and with the substantial absence of grit. In particular, there is a need for a process for preparing stable, high solids, dispersions of microcomposite particles having polymer particles adsorbed onto a inorganic material particle.

In particular, there is a continuing need to improve the effective utilization of titanium dioxide in aqueous coating compositions and thereby to improve the opacity and other performance properties of coating compositions. In addition, there is a need for a method of minimizing the viscosity of titanium dioxide slurries, and to quickly prepare such slurries. Further, there is a need for a process to disperse titanium dioxide particles at high concentrations in coating compositions with a minimal amount of dispersing surfactant and with the substantial absence of grit. In particular, there is a need for a process for preparing stable, high solids, dispersions of microcomposite particles having polymer particles adsorbed onto a titanium dioxide particle.

According to a first aspect of the present invention there is provided a process for forming a suspension of discrete composite particles, each composite particle comprising an ~~insoluble first particle~~ and at least one insoluble ~~second particle on the surface of the first particle~~, comprising mixing the first particles

with the second particles under conditions to form a suspension substantially free of agglomerates comprising multiple first particles and agglomerates consisting of just multiple second particles; wherein the conditions are such that the mixture is only slightly unstable towards heteroagglomeration of the first and second particles.

According to a second aspect of the present invention there is provided a suspension of at least 10% solids of composite particles obtainable by a process according to the first aspect of the present invention.

. . . . The present invention allows for the formation of composite particles each comprising a plurality of second particles on the surface of a first particle. In the present process, the second particles can be inorganic and/or organic and the first particle can be inorganic or organic.

In order to explain more fully the present invention it should be appreciated that suspensions of discrete particles do not behave in a uniform manner. Some suspensions are stable in that the particles retain their discrete state (e.g.  $\text{TiO}_2$  particles stabilized with adsorbed soluble polyelectrolyte dispersants). Some suspensions are unstable in that multi-particle agglomerates form (e.g. unstabilized  $\text{TiO}_2$  particles and clay particles). The formation of multi-particle agglomerates is attributable to a number of factors such as different particle surface changes and different ~~Van De Waal's forces~~ between particles. The degree of instability and the rate of multi-particulate formation is related to the relative magnitude of these factors. In many applications, the formation of multi-particle agglomerates is highly undesirable (e.g. paints).

Agglomerate formation can be pictorially represented as Scheme A in Figure 1a. This Scheme would be typical for unstabilized  $\text{TiO}_2$  multi-particle agglomerate formation.

For mixture particle suspensions, the formation of multi-particle heteroagglomerates can be represented as Scheme B in Figure 1a. These types of heteroagglomerates contain multi-first particles and multi-second particles. The formation of these multi first heteroagglomerates can be shown qualitatively by comparing simple energy diagrams of the type shown in Figure 1b. In this

Figure, the energy barrier in the stable condition is too high for agglomerates to form. This is not the case in the unstable condition.

In the present invention, first and second particles are mixed together. However, instead of the particles forming multi-first and multi-second particles (i.e. following Scheme B), the particles form discrete first and second composite particles wherein each composite particle has one first particle and at least one second particle on the surface of the first particle. The present invention can be represented as Scheme C in Figure 1a. The discrete composite particles of the present invention are formed by tailoring the conditions such that the mixture is only slightly unstable towards hetero-agglomeration of the first and second particles.

The formation of the hetero-agglomerates of the present invention can be shown qualitatively by comparing more complex (but more representative) energy diagrams that allow for the formation of intermediate states, such as the diagrams shown in Figure 1c. In this Figure, each energy diagram shows the possible transition of an initial state through to a final state via an intermediate state.

In the stable condition, the energy barrier to reach the intermediate state (intermediate energy barrier) is too high for either the intermediate state or the final state to form.

In the unstable state, the intermediate energy barrier is low enough to form the intermediate state. However, the energy barrier to reach the final state (final energy barrier) is also low and to such an extent that the intermediate state itself is so unstable that it forms the final state.

In the only slightly unstable conditions of the present invention, the intermediate energy barrier is higher than the unstable condition but is still low enough to allow for the formation of the intermediate state (i.e. the heteroagglomerates of the present invention). However, the final energy barrier is too high to allow for the formation of the final state and thus provides for the stabilisation of the intermediate state. In the present invention, the conditions are tailored so that the intermediate energy barrier is higher than it would be under unstable conditions. The final energy barrier is high enough to stabilise

the intermediate state (i.e. the particles of the present invention).

The formation a suspension of composite particles comprising one first particle (some times refered to as a core particle) and at least one second particle on the surface of the first particle wherein the suspension is free of multi first agglomerates or agglomerates consisting of just second particles is unexpected. Normally, one would have expected the formation of multiple first and second particle agglomerates (i.e. agglomerates formed by Scheme B). Up until the present invention, it was never recognised or appreciated that one could ever control, let alone how to control, conditions to allow for the formation of the suspension of the present invention.

Preferably, the first particles are the same and the second particles are the same. For example, all of the first particles can be either inorganic or organic particles and all of the second particles can be either inorganic or organic particles.

Preferably, the first particles or the second particles are ~~inorganic particles~~ and the other of the first particles or the second particles are ~~organic particles~~.

Preferably, the inorganic particles are  $\text{TiO}_2$  particles.

Preferably, the organic particles are polymer latex particles.

Preferably, the first and second particles have the same sign of surface charge. For example, the sign is either positive or negative or zero.

Preferably, the surface potential of each first particle is different from the surface potential of each second particle.

Preferably, either the first particles or the second particles comprise a chemical group for attachment to the other of the first particles or the second particles. The term attachment includes (but is not limited to) attachment by adsorption and attachment by a chemical reaction.

Preferably, the chemical group is a polymerizable ethylenically unsaturated acid-functional monomer. Preferably, the polymerizable ethylenically unsaturated acid-functional monomer is any one of itaconic acid; and a dihydrogen phosphate ester of an alcohol containing a polymerizable olefinic group. Preferably, the dihydrogen phosphate ester is selected from the

phosphoric acid monoester of 2-hydroxyethyl methacrylate, the phosphoric acid diester of 2-hydroxyethyl methacrylate, the phosphoric acid monoester of 3-hydroxypropyl methacrylate, and the phosphoric acid diester of 3-hydroxypropyl methacrylate. Preferably, the at least one polymerizable dihydrogen phosphate-functional monomer is selected from the dihydrogen vinylbenzyl- phosphates, and  $\text{CH}_2=\text{CCH}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{OPO}(\text{OH})_2$ ,  $\text{CH}_2=\text{CCH}_3\text{CO}_2\text{CH}_2\text{CH}[\text{OPO}(\text{OH})_2]\text{CH}_3$ ,  $\text{CH}_2=\text{CCH}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OPO}(\text{OH})_2$ , and  $\text{CH}_2=\text{CCH}_3\text{CO}_2\text{CH}_2\text{CHOHCH}_2\text{OPO}(\text{OH})_2$ .

Preferably, a pigment dispersant is present. A preferred pigment dispersant is a polyelectrolyte. Preferably, the pigment dispersant is selected from poly(meth)acrylic acid, poly(meth)acrylic acid salts, polyelectrolyte copolymers of (meth)acrylic acid and salts of polyelectrolyte copolymers of (meth)acrylic acid. The pigment dispersant may be an inorganic polyelectrolyte. Preferably, the pigment dispersant is a polyphosphate salt.

The present invention therefore relates to a process for forming a suspension of discrete composite particles, each composite particle comprising an insoluble first particle and at least one insoluble second particle on the surface of the first particle, comprising mixing the first particles with the second particles under conditions to form a suspension substantially free of agglomerates comprising multiple first particles and agglomerates consisting of just multiple second particles; wherein the conditions are such that the mixture is only slightly unstable towards heteroagglomeration of the first and second particles. The process is applicable for absorbing inorganic particles onto an inorganic particle, absorbing organic particles onto an organic particle, absorbing inorganic particles onto an organic particle, and absorbing organic particles onto an inorganic particle. The present invention also provides for the formation of composite particles of the type just described adsorbed on a third particle, which may be organic or inorganic in nature.

In a preferred embodiment, the present invention is directed to a process for preparing an aqueous dispersion of composite particles, each composite particle comprising a plurality of polymeric latex particles adsorbed to an

inorganic material particle (such as clay, silica, calcium carbonate,  $\text{TiO}_2$ ), the process comprising: a) suspending inorganic material particles in an aqueous medium; b) suspending the polymeric latex particles in an aqueous medium, the sign of the surface charge of the polymeric latex particles being the same as the sign of the surface charge of the inorganic material particles, the zeta potential of the polymeric latex particles in the aqueous medium being greater in absolute value than the zeta potential of the inorganic material particles in the aqueous medium; and c) mixing the aqueous medium/media containing the inorganic material particles and the polymeric latex particles.

In another preferred embodiment, the present invention is directed to a process for preparing an aqueous dispersion of composite particles, each composite particle comprising a plurality of polymeric latex particles adsorbed onto an inorganic material particle (such as clay, silica, calcium carbonate,  $\text{TiO}_2$ ), the process comprising: a) suspending inorganic material particles in an aqueous medium, b) suspending the polymeric latex particles in an aqueous medium, the polymeric latex particles being stabilized against homocoagulation by polymeric steric stabilization, the surface potential of one of either of the polymeric latex particles or the inorganic material particles in the aqueous medium being greater in absolute value than the surface potential of the other of the polymeric latex particles and the inorganic material particles; and c) mixing the aqueous medium/media containing the inorganic material particles and the polymeric latex particles, the polymeric latex particles adsorbing onto the inorganic material particles to provide the composite particles.

In a preferred embodiment, the invention is directed to a process for preparing an aqueous dispersion of composite particles, each composite particle comprising a plurality of polymeric latex particles adsorbed onto an inorganic material particle (such as clay, silica, calcium carbonate,  $\text{TiO}_2$ ) the process comprising: a) suspending inorganic material particles in an aqueous medium; b) suspending the polymeric latex particles in the aqueous medium, the sign of the surface charge of the polymeric latex particles being the same as the sign of the surface charge of the inorganic material particles, the surface potential of one



of either of the polymeric latex particles or the inorganic material particles in the aqueous medium being greater in absolute value than the surface potential of the other of the polymeric latex particles and the inorganic material particles; and c) mixing the aqueous medium/media containing the inorganic material particles and the polymeric latex particles, the polymeric latex particles adsorbing onto the inorganic material particles to provide the composite particles.

In another preferred embodiment, the present invention relates to a process for preparing an aqueous dispersion of composite particles, each composite particle comprising a plurality of polymeric latex particles (which may be dispersant latex particles) adsorbed onto an inorganic material particle (such as  $\text{TiO}_2$ , clay, calcium carbonate, silica), the process comprising: a) suspending polymeric latex particles in an aqueous medium, the polymeric latex particles having been polymerized in the absence of the inorganic material particles; b) suspending inorganic material particles in an aqueous medium (which may be the same medium as the first medium), the sign of the surface charge of the polymeric latex particles being the same as the sign of the surface charge of the inorganic material particles, the surface potential of one of either of the polymeric latex particles or the inorganic material particles in the aqueous medium being greater in absolute value than the surface potential of the other of the polymeric latex particles and the inorganic material particles; and c) mixing the aqueous media/medium containing the inorganic material particles and the polymeric latex particles in the absence of conditions providing gross heterocoagulation, the polymeric latex particles adsorbing onto the inorganic material particles to provide the composite particles.

In another preferred embodiment, the present invention relates to a process for preparing an aqueous composition, the composition including dispersed composite particles, each composite particle comprising a plurality of polymeric latex dispersant particles adsorbed to a inorganic material particle, the process comprising: a) suspending inorganic material particles in an aqueous medium; b) suspending the polymeric latex particles in an aqueous medium, the polymeric latex particles being stable with respect to homocoagulation; and c) mixing the

aqueous medium/media containing the inorganic material particles and the polymeric latex particles, the mixture including the inorganic material particles and the polymeric latex particles being unstable with respect to heterocoagulation, the energy barrier with respect to heterocoagulation of the polymeric latex particles and the inorganic particles being sufficiently great so that rapid heterocoagulation forming a substantial proportion by weight of aggregates including multiple inorganic material particles is avoided, the polymeric latex particles adsorbing onto the inorganic material particles to provide the composite particles.

In another preferred embodiment, the present invention relates to a process for preparing an aqueous dispersion of composite particles, the composite particles each comprising a plurality of selected polymeric latex particles adsorbed onto an inorganic material particle, the process comprising: a) preparing a dispersion or suspension of polymeric latex particles in an aqueous medium, the polymeric latex particles having a surface potential (zero, negative or positive, preferably negative) and being prepared by a preparative emulsion polymerization process in the absence of inorganic material particles, the preparative emulsion polymerization process being selected from the class consisting of: 1) emulsion polymerization processes employing a monomer mixture including at least one polymerizable ethylenically unsaturated acid-functional monomer, the at least one polymerizable ethylenically unsaturated acid-functional monomer being selected from the class consisting of: A) itaconic acid; and B) dihydrogen phosphate esters of an alcohol, the alcohol containing a polymerizable olefinic group; 2) emulsion polymerization processes preferentially providing acid-functionality proximate the surface of the polymeric latex particle; and 3) emulsion polymerization processes employing a monomer mixture including at least one ethylenically unsaturated acid-functional monomer, the total weight of ethylenically unsaturated acid-functional monomer comprising at least about ten percent by weight of the polymeric latex solids; b) suspending inorganic material particles in an aqueous medium (which may be the same aqueous medium), the inorganic material particles having a surface potential in the aqueous medium (zero, negative or

positive, preferably being the same as the latex particles and more preferably being less than the latex particles), the surface potential of the inorganic material particles and the polymeric latex particles stabilizing the inorganic material particles and the polymeric latex particles against gross heterocoagulation, the polymeric latex particles being selected, by the use of the preparative emulsion polymerization process, to adsorb onto the inorganic material particles in a controlled manner, and c) mixing the aqueous medium/media containing the inorganic material particles and the selected polymeric latex particles, the selected polymeric latex particles adsorbing onto the inorganic material particles to provide the composite particles.

Preferably, the surface potential of the polymeric latex particles in the aqueous medium is greater in absolute value than the surface potential of the inorganic material particles in the aqueous medium.

Preferably, the zeta potential of the inorganic material particles is negative. Preferably, the zeta potential of the inorganic material particles is more negative than about -5 mv. Preferably, the zeta potential of the polymeric latex particles is more negative than about -20 mv. Preferably, the zeta potential of the inorganic material particles is from about -5 mv to about -70 mv, the zeta potential of the polymeric latex particles being from about -20 mv to -120 mv. Preferably, the zeta potential of the inorganic material particles is from about -20 mv to -60 mv, the zeta potential of the polymeric latex particles being from about -40 mv to about -110 mv. Preferably, the product of the zeta potential of the inorganic material particles and the zeta potential of the polymeric latex particles is from about 100 mv<sup>2</sup> to 8400 mv<sup>2</sup>. Preferably, the absolute value of the difference in the zeta potential of the inorganic material particles and the the zeta potential of the polymeric latex particles is at least about 30 mv. Typical difference values are around 35 mv for particles such as silane treated silica and polymeric latex particles, between around 38 mv to 42 mv for particles such as clay and the polymer Rhoplex TR-407 over the pH range of from 4.2 to 2.9 (Rhoplex is a trade mark of Rohm and Haas Company), and between around from 45 mv to 50 mv for particles such as TiO<sub>2</sub> and the polymer Rhoplex AC-61 (Rhoplex is a trade

mark of Rohm and Haas Company. Preferably, the zeta potential of the polymeric latex particles is attributable to ionized acid functionality at the surface of the polymeric latex particles.

Preferably, the process further comprises adjusting the zeta potential of the inorganic material particle surface prior to mixing the aqueous medium containing the inorganic material particles and the polymeric latex particles. When the inorganic material particles are clay, the zeta potential of the inorganic material particles is adjusted by addition of an aminosilane compound, acid or aluminium sulfate. When the inorganic material particles are silica, the zeta potential of the inorganic material particles is adjusted by addition of an aminosilane compound. Preferably, the aminosilane compound is 2-aminoethyl-3-aminopropyl-trimethoxysilane. When the inorganic material particles are calcium carbonate, the zeta potential of the inorganic material is adjusted by addition of less than about 0.2 percent by weight of calcium carbonate solids of an anionic polyelectrolyte.

Preferably, the energy barrier with respect to heterocoagulation of the polymeric latex particles and the inorganic particles is sufficiently great so that rapid heterocoagulation forming a substantial proportion by weight of aggregates including multiple inorganic material particles is avoided. Preferably, the energy barrier with respect to heterocoagulation is at least about 3 kT. Preferably, the energy barrier with respect to heterocoagulation is less than about 10 kT.

Preferably, the polymeric latex particles are stable with respect to homocoagulation. Preferably, the polymeric latex particles are stabilized against homocoagulation by polymeric steric stabilization.

Preferably, the inorganic material particle has a saturation level for adsorption of the polymeric latex particles and the proportion of polymeric latex particles in the aqueous medium is at least great enough to provide composite particles having polymeric latex particles at the saturation level.

Preferably, the average size of the polymeric latex particles is from about 20 nm to about four times the average particle size of the inorganic material particles. Preferably, the average size of the polymeric latex particles is from about 50 nm the average size of the inorganic material particles to about equal to the average

size of the inorganic material particles. Preferably, the average particle size of the inorganic material particles is from about 100 nm to 10,000 nm, and the average size of the polymeric latex particles is from about 20 nm to 5000 nm. Preferably, the inorganic material particles are titanium dioxide particles and the average particle size of the inorganic material particles is from about 200 nm to 250 nm, the average size of the polymeric latex particles being from about 20 nm to 1000 nm (preferably 250 nm). Preferably, the average size of the polymeric latex particles is from about one-quarter the average size of the titanium dioxide particles to about equal to the average size of the titanium dioxide particles.

Preferably, the aqueous medium containing the inorganic material particles and the polymeric latex particles is substantially free of polyelectrolyte dispersants. Preferably, the aqueous medium containing the inorganic material and the polymeric latex particles includes no more than about 0.2 percent by weight poly-electrolyte dispersant based on the weight of inorganic material, particularly if the inorganic material is titanium dioxide.

Preferably, the process further comprises preparing polymeric latex particles by an emulsion polymerization process from monomer mixture including at least one polymerizable ethylenically unsaturated acid-functional monomer. Preferably, the polymeric latex particles are prepared by an emulsion polymerization process which preferentially provides acid functionality at the surface of the polymeric latex particles. Preferably, the polymeric latex particles being polymerized from monomer including at least one polymerizable dihydrogen phosphate-functional monomer. Preferably, the at least one polymerizable ethylenically unsaturated acid- functional monomer is a dihydrogen phosphate ester of an alcohol, the alcohol containing a polymerizable vinyl or olefinic group (polymerizable non-vinyl olefinic groups). Preferably, the dihydrogen phosphate ester is selected from the phosphoric acid monoester of 2-hydroxyethyl methacrylate, the phosphoric acid diester of 2-hydroxyethyl methacrylate, the phosphoric acid monoester of 3-hydroxypropyl methacrylate, and the phosphoric acid diester of 3-hydroxypropyl methacrylate, and the dihydrogen phosphate monoester of 2-hydroxyethyl methacrylate, and mixtures of the dihydrogen phosphate monoester of 2-hydroxyethyl

methacrylate and the phosphoric acid diester of 2-hydroxyethyl methacrylate. Preferably, the at least one polymerizable dihydrogen phosphate-functional monomer is selected from the dihydrogen vinylbenzylphosphates, and  $\text{CH}_2=\text{CCH}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{OPO}(\text{OH})_2$ ,  $\text{CH}_2=\text{CCH}_3\text{CO}_2\text{CH}_2\text{CH}[\text{OPO}(\text{OH})_2]\text{CH}_3$ ,  $\text{CH}_2=\text{CCH}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OPO}(\text{OH})_2$ , and  $\text{CH}_2=\text{CCH}_3\text{CO}_2\text{CH}_2\text{CHOHCH}_2\text{OPO}(\text{OH})_2$ .

Preferably, the polymeric latex particles are polymerized from monomer including itaconic acid.

Preferably, the effective glass transition temperature of the polymeric latex particles is less than about  $60^\circ\text{C}$ . Preferably, the effective glass transition temperature of the polymeric latex particles is greater than about  $50^\circ\text{C}$ .

Preferably, the process further comprises mixing an aqueous dispersion of polymeric latex binder particles with the aqueous medium containing the dispersed composite particles. Preferably, the polymeric latex binder particles and the polymeric latex dispersant particles are the same.

Preferably, the latex particles are polymeric latex dispersant particles.

Preferably, the total solids of the aqueous medium containing the inorganic material particles and polymeric latex particles is greater than about 10 percent by weight.

Preferably, a pressure sensitive adhesive composition is produced. Preferably, a coatings composition is produced. Preferably, a paper coating composition is produced. Preferably, the process further comprises applying the aqueous dispersion of composite particles to a fiberfill material to coat the fiberfill material to provide a bound fiberfill material. Preferably, the process further comprises coating a non-woven or textile material with the dispersion. Preferably, the process additionally comprises frothing the dispersion before coating the material. Preferably, an inorganic material slurry is produced.

The present invention therefore provides a process for preparing an aqueous dispersion of composite particles, the composite particles each including a plurality of polymeric latex particles adsorbed onto an inorganic material particle. The resulting composite particles can be used in preparing formulated

aqueous compositions, such as coating compositions, adhesives, binders, for non-woven materials, and paints, which in turn give coatings and other products in which the inorganic material is more efficaciously dispersed than in prior art formulations. The improved dispersion of the inorganic material particles provided by the process of the present invention advantageously provides greater flexibility in preparing aqueous compositions including dispersed inorganic material. For example, in some cases the present process provides a means of reducing the amount of inorganic material required to provide desired properties, such as mechanical properties or opacification. In other cases, in which the inorganic material is inexpensive, the present process provides a means of increasing the amount of inorganic material which can be included in an aqueous composition to reduce cost while maintaining performance properties.

The improved dispersion of the titanium dioxide particles provided by the process of the present invention advantageously reduces the amount of titanium dioxide required to provide desired coating properties, such as opacity or hiding, tint strength, mechanical properties, "ICI" or "cone-and-plate" (high shear rate) viscosity, gloss, and scub resistance. The process also provides coating compositions giving coatings with improved opacity for a given pigment level.

In a preferred embodiment, the process of the present invention employs controlled adsorption of polymeric latex particles onto inorganic material particles to provide composite particles. Adsorption conditions are selected to provide composite particles including adsorbed polymer latex particles, preferably at a saturation level on the inorganic material particles, while formation of composite particles including more than single inorganic material particles, and higher levels of inorganic material particle aggregation, is substantially avoided. Thus, conditions are chosen such that a mixture of the inorganic material particles and the polymeric latex particles is just slightly unstable with respect to formation of composite particles, the values of parameters characterizing the stability of the system lying in a relatively narrow range between those characteristic of stability and those characteristic of instability with respect to aggregation. By operating in this narrow range of slight

instability a slow, controlled heterocoagulation to well-dispersed composites is effected and the rapid heterocoagulation leading to substantial aggregates of inorganic material particles is avoided. The stability of the mixture with respect to adsorption can be adjusted in a number of ways. For example, the relative surface potential of the inorganic material particles and the polymeric latex particles can be varied. The stability of the mixture can also be varied by adsorbing a carefully established level of a polyelectrolyte such as a pigment dispersant onto the surface of the inorganic material particles. The inorganic material particles are most frequently stabilized by surface charge, but can also be stabilized by steric forces, or by a combination of surface charge and steric forces.

Preferably, in one embodiment the polymeric latex particles are polymerized from monomer which provides polymer which is hard or rigid at the temperature at which the composite particles are to be used, such as monomer which provides a polymeric material with an effective glass transition temperature of at least about 50°C in the case of a composition including composite particles and applied at ambient or room temperature (that is, at about 20- 23°C). The rigidity of the adsorbed polymeric latex particles is believed to aid in spacing adjacent inorganic material particles.

However, in another embodiment of the present invention, the polymeric latex particles are polymerized from monomer which provides a polymeric material which is soft and deformable under the conditions in which the composition including the composite particles is used. For example, the effective glass transition temperature of the polymeric latex particles in this case can be from about 0°C to 20°C, and the adsorbed polymeric latex particles serving as a binder for the composition. Surprisingly, even though the polymeric latex particles are formed from a soft, deformable material, an improvement in application performance properties, such as hiding, can be observed.

In a presently preferred embodiment, the process of the present invention comprises: a) suspending inorganic material particles in an aqueous medium; b) suspending the polymeric latex particles in the aqueous medium, the sign of the surface charge of the polymeric latex particles being the same as the sign of the surface charge of the inorganic material particles, the surface potential of one of



either of the polymeric latex particles or the inorganic material particles in the aqueous medium being greater in absolute value than the surface potential of the other of the polymeric latex particles and the inorganic material particles; and c) mixing the aqueous medium containing the inorganic material particles and the polymeric latex particles, the polymeric latex particles adsorbing onto the inorganic material particles to provide the composite particles.

The inorganic material particles and the polymeric latex particles can be mixed in any order, and in the same or different aqueous medium. When inorganic material particles are suspended in an aqueous medium which already includes the polymeric latex particles, as when inorganic material pigment is ground in an aqueous medium including polymeric latex particles as a pigment dispersant, greater volume solids can be achieved than otherwise.

In another embodiment, the process of the present invention employs polymeric latex particles which are sterically stabilized, in this case the process comprises: a) suspending inorganic material particles in an aqueous medium; b) suspending the polymeric latex particles in the aqueous medium, the polymeric latex particles being stabilized against homocoagulation by polymeric steric stabilization, the surface potential of one of either of the polymeric latex particles or the inorganic material particles in the aqueous medium being greater in absolute value than the surface potential of the other of the polymeric latex particles and the inorganic material; c) mixing the aqueous medium containing the inorganic material particles and the polymeric latex particles, the polymeric latex particles adsorbing onto the inorganic material particles to provide the composite particles.

Both the case of surface charge stabilization and the case of steric stabilization, as well as the case of mixed surface charge and steric stabilization, are encompassed by expressing the process of this invention in terms of energy criteria. In those terms, the process of the present invention comprises: a) suspending inorganic material particles in an aqueous medium; b) suspending the polymeric latex particles in the aqueous medium, the polymeric latex particles being stable with respect to homocoagulation; and c) mixing the aqueous medium containing the inorganic material particles and the polymeric

latex particles, the mixture including the inorganic material particles and the polymeric latex particles being unstable with respect to heterocoagulation, the energy barrier with respect to heterocoagulation of the polymeric latex particles and the inorganic material being sufficiently great so that rapid heterocoagulation forming a substantial proportion by weight of aggregates including multiple inorganic material particles is avoided, the polymeric latex particles adsorbing onto the inorganic material particles to provide the composite particles.

In this latter case, it is preferred that the energy barrier with respect to heterocoagulation be less than about 10 kT, and more preferably the energy barrier with respect to heterocoagulation be at least about 3 kT. Under these conditions, the inorganic material particles may be slightly unstable with respect to homocoagulation, and such homocoagulation may to some extent compete with the process of the present invention. However, the polymeric latex particles are preferably present in greater relative number concentrations than the inorganic material particles. This greater relative concentration and the shear of mixing of the aqueous medium containing both the inorganic material particles and the polymeric latex particles is believed to favor ultimate formation of the composite particles over the formation of aggregates of the inorganic material particles.

The composite particles formed by the process of the present invention are themselves stable with respect to homocoagulation.

The inorganic material particles have a characteristic maximum level for adsorption of the polymeric latex particles. This adsorption saturation level can be determined empirically, and is believed to depend on a number of factors including geometric factors relating to the relative sizes and shapes of the inorganic material and polymeric latex particles. Preferably, the proportion of polymeric latex particles in the aqueous medium employed in the present process is at least great enough to provide composite particles having polymeric latex particles at this saturation level. This advantageously enhances the stability of the composite particles formed.

In practicing the first presently preferred embodiment of the process of the

present invention, the aqueous medium containing the inorganic material particles and the polymeric latex particles is generally preferred to be substantially free of polyelectrolyte dispersants. These polyelectrolyte dispersants, such as potassium tripolyphosphate, polyacrylic acid, polymethacrylic acid, and the like, which are often used as dispersion aids in preparing a pigment grind, are believed to adsorb to the surface of the inorganic material in the grind, and thus increase the absolute value of the frequently negative surface charge density of the pigment particles by making the surface potential more negative.

The effect of this if too much is used can be to excessively increase electrical repulsive forces between inorganic material particles and polymeric latex particles, thus reducing or even precluding the adsorption of the polymeric latex particles onto the inorganic material particles.

In one aspect of the present invention, irreversibly adsorbing polymeric latex particles are prepared and used in the presence of such polyelectrolyte dispersants. Alternatively, the level of polyelectrolyte dispersant in the grind is reduced permitting a wide variety of polymeric latex particles to be used in the process of this invention, including many commercially available latexes. In this latter case, preferably, the aqueous medium containing the inorganic material particles and the polymeric latex particles includes no more than a low level, such as about 0.2 percent by weight, of the polyelectrolyte dispersant based on the weight of the inorganic material. In some cases, including low levels of polyelectrolyte dispersant is preferred to reduce grit formation, the low levels of polyelectrolyte dispersant being believed to provide additional surface charge density or surface potential on the inorganic material particles, and reducing the rate of undesirable aggregation and grit formation, which may otherwise tend to result in aggregates including multiple inorganic particles.

The process of the present invention advantageously permits dispersion of inorganic material particles using polymeric latex particles at high inorganic material concentrations. In particular, the process can be carried out so that the inorganic material particles comprise at least about five percent by volume of the components of the mixture or pigment grind. However, the process of the present invention can be employed in compositions typically including low

levels of specific inorganic material particles, such as titanium dioxide particles in mastic and caulk compositions in which the titanium dioxide particles have a PVC of about two to three percent.

The process of the present invention further contemplates preparing fully formulated aqueous compositions, including aqueous coating, adhesive and binder compositions, using the composite particles formed by adsorption of the polymeric latex particles onto the inorganic material particles, and the subsequent use of the fully formulated aqueous compositions to form products, including coatings, adhesives and binders, and articles made using these products, such as coated articles, bound fiberfill articles, coated paper and boardstock, and the like. While the aqueous medium containing the composite particles can be used directly in some cases to form products, in many instances it is desirable to employ the aqueous medium including the composite particles as an intermediate in the production of an aqueous composition, such as a coating, adhesive or binder composition, including one or more additional components (a "fully formulated" composition).

The present process provides for the controlled adsorption of the polymeric latex on the surface of the inorganic material to yield concentrated, stable dispersions. The composite particles resulting from this controlled adsorption process are particularly useful for improving the performance properties and permeability of coatings, films, adhesives and binders formed therefrom. Alternatively, the availability of the controlled adsorption process of the invention offers the ability to formulate coatings and films of substantially equal performance properties as conventional systems but with lower concentrations of expensive inorganic materials and accordingly at lower cost. Further, the present process advantageously provides a means of quickly preparing low viscosity slurries of highly concentrated inorganic material as an intermediate for use in a variety of applications. In addition, the present process permits low cost inorganic material particles to be dispersed in certain adhesives and binders which conventionally have not included such materials, because their presence significantly degraded important performance properties. Similarly, the present process permits low cost inorganic material particles to be dispersed at even

higher levels than otherwise in some systems, further reducing product raw material costs.

In one preferred embodiment, the process of the present invention employs the selection of properties of polymeric latexes for use in controlled adsorption onto inorganic material particles. In addition, the process optionally provides for the adjustment of the properties of the inorganic material particles themselves. The process provides a solution to the problem of how to practically utilize polymeric latex particles and inorganic material particles to improve the distribution and stability of the inorganic material particles in aqueous-based coatings, paints, mastics, caulks, adhesives and binders for non-woven materials containing high concentrations of inorganic material particles.

Polymeric latex particles of selected composition, size and surface charge can be effectively used in the process of the present invention to disperse inorganic material particles in concentrated dispersions. The selected polymeric latex particles function in the process by adsorbing onto the surface of the inorganic material particles in a controlled manner. The terminology "controlled" is used herein to distinguish heterocoagulation involving stepwise accretion of polymeric latex particles on inorganic material particles from gross heterocoagulation of the entire system, such as often occurs when positively and negatively charged particles are mixed. By "controlled" is meant not only that does the selected polymeric latex or polymer latexes adsorb onto the surface of the inorganic material particles but also that the dispersion formed therefrom is stable, and that the adsorption is accomplished in such a manner so as to provide a "monolayer"; in the dried film this monolayer of polymeric latex efficiently spaces apart the inorganic material particles so as to permit them to provide improved performance properties in the final coating, film, adhesive or binder.

As distinguished from prior art processes in which polymerization takes place in the presence of and/or on the surface of inorganic particles, the process of a preferred embodiment of the present invention utilizes selected, separately formed, polymeric latex particles to improve the dispersion and distribution of concentrated inorganic material particles in polymer compositions, including dried films formed from aqueous coating compositions, from aqueous adhesive

compositions, from aqueous binder compositions for non-woven materials, and the like. More particularly, the process provides means for improving the dispersion and distribution of inorganic material pigment particles, such as those present at concentrations of at least about ten percent by volume of the mixture during formation of the composite particles, by adsorption of at least one selected, separately polymerized, polymeric latex onto the inorganic material particles, thereby forming a stable dispersion of microcomposite particles, rather than aggregates or flocculates as might be expected employing prior art processes.

The present process provides for the controlled adsorption of the polymeric latex on the surface of the inorganic material in concentrated, stable dispersions. The composite particles resulting from this controlled adsorption process are particularly useful for improving the permeability, and optical and mechanical properties including the opacity, gloss, color development, high shear viscosity and scrub resistance, of coatings, films, mastics, caulks, binders, and adhesives formed therefrom. Alternatively, the controlled adsorption process of the invention offers the ability to formulate coatings, films, adhesives and binders of substantially equal performance properties as conventional systems but with lower inorganic material particle concentrations if desired. Further, the present process advantageously provides a means of quickly preparing low viscosity slurries of highly concentrated inorganic material as an intermediate for use in a variety of applications. In addition, the present process permits low cost inorganic material particles to be dispersed in certain adhesives and binders which have conventionally omitted such materials, because their presence previously significantly degraded important performance properties. Similarly, the present process permits low cost inorganic material particles to be included at even higher levels in some compositions than would otherwise be possible without sacrificing important performance properties, further reducing the total cost of raw materials for these compositions.

A number of factors relate to and can affect the adsorption of polymeric latex particles to inorganic material particles. These factors include the characteristics of the polymeric latex particles, of the inorganic material particles, and of the aqueous medium used in the process of the invention. For example, with

respect to the polymeric latex particles, these factors include the monomer composition, the particle size, and particle size distribution, and surface potential or surface charge density, as well as the nature and proportion of functional groups, such as acid groups including, for example, carboxylate and phosphate groups at the particle surface; with respect to the inorganic material particles, the factors include the particle size, particle size distribution, surface potential or surface charge density of the particles, and whether there are other species adsorbed on the surface, such as polyelectrolyte dispersants and/or polymeric steric stabilization agents; with respect to the medium, the pH, the ionic content of the medium, and the dielectric constant can all be significant, as can the concentration and nature of other surface active substances present in the medium, such as pigment dispersants and surfactants.

In some cases a commercially available polymeric latex has suitable properties and can be selected for use in the process of this invention. In other cases, it may be desirable to modify an existing polymeric latex so that it possesses these properties. In still other cases, a special polymeric latex can be prepared for use in the process of this invention.

Similarly, some commercial grades of inorganic material can be dispersed in the process of this invention without prior treatment or modification. However, there may be some situations in which it is desirable to treat or modify the inorganic material particles before dispersion is attempted. For example, it may be desirable to adsorb a small molecular species such as an anionic surfactant to modify the surface charge density of the inorganic material (that is, by making the surface charge density more negative and thus raising its absolute value) before the dispersion is carried out. Similarly, a cationic material could be adsorbed to make the surface charge density of the inorganic material less negative. In other cases, such as in the case of titanium dioxide, it may be desirable to select a commercially available grade of the inorganic material particles with an appropriate inorganic material surface treatment (such as surface silica or alumina on titanium dioxide particles) to give a desired surface potential. In some cases, it may be desirable to adsorb a polyelectrolyte dispersant or a polymeric steric stabilization agent onto the surface of the inorganic material

particles.

In addition, it may be desirable to modify the aqueous medium used, such as by adjusting the pH to provide the desired zeta potentials on the particles, by addition of salts to increase the ionic strength of the medium, or the like. Further, modification of the aqueous medium before dispersion of the inorganic material, or subsequent to that dispersion, can be accomplished by addition of surface active agents such as conventional polyelectrolyte pigment dispersants or anionic surfactants, or the like, with the understanding that such surface active agents may adsorb to the inorganic material particles and change their effective surface potential. Modification of the medium may also occur as an incident to steps taken to modify the surface properties of the polymeric latex or the inorganic material particles.

In a first presently preferred embodiment of the process of this invention the polymeric latex particles which are adsorbed have a surface charge with the same sign as the surface charge of the inorganic material particles. Usually, both the polymeric latex particles and the inorganic material particles will have a negative surface charge. One of either the polymeric latex particles or the inorganic material particles can have a surface potential which is greater in absolute value than the other of the polymeric latex particles and the inorganic material particles. For example, the polymeric latex particles can have a surface potential in the aqueous medium which is greater in absolute value than the surface potential of the inorganic material particles. In prior art processes in which the polymeric latex particles and the inorganic particles have surface charges with opposite signs, uncontrollable aggregation typically occurs, especially at high particle concentrations. This is not the case with the present invention.

Depending on other factors, such as the presence and nature of polyelectrolyte dispersant and/or polymeric steric stabilization agent adsorbed on the surface of the inorganic material particles, and the absolute value of the difference in surface potential between the inorganic material particles and the polymeric latex particles, the signs of the surface charges on the inorganic material particles and the polymeric latex particles can differ. For example, under some conditions the surface potential of the inorganic material particles can be slightly positive, while



the surface potential of the polymeric latex particles is sufficiently negative so that the resulting composite particles have a stabilizing negative surface potential.

Thus, it can be seen that the present invention provides a process for preparing an aqueous composition including dispersed composite particles in which inorganic material particles are suspended in an aqueous medium, the inorganic material particles being slightly unstable with respect to homocoagulation, while also suspending the polymeric latex particles in the aqueous medium, the polymeric latex particles being stable with respect to homocoagulation. However, the mixture including the inorganic material particles and the polymeric latex particles is unstable with respect to heterocoagulation and the resultant formation of composite particles having polymeric latex particles adsorbed onto inorganic material particles. Mixing the aqueous media including both the inorganic material particles and the polymeric latex particle is believed to favor hetero-coagulation forming composite particles over formation of homo-aggregates of inorganic material particles. Yet, the energy barrier with respect to heterocoagulation of the polymeric latex particles and inorganic material particles is sufficiently great so that rapid heterocoagulation forming a substantial proportion by weight (such as about one percent by weight of total solids) of aggregates including multiple inorganic material particles is avoided.

The weight of aggregated material including multiple inorganic material particles ("grit") which is acceptable depends greatly on the properties required in the fully aqueous compositions. For example, when the dispersed composite particles prepared by the controlled adsorption effected by the process of the present invention are formulated into high gloss aqueous coating compositions, even very low levels of macroscopic aggregation leading to grit can significantly detract from the appearance of the coated article. This effect can be gauged readily by visual observation, either directly or with the aid of a low powered optical microscope, of a dried film prepared by drawing down a smooth layer of the high gloss aqueous coating over an impervious substrate. In cases of severe grit, the dried coating will display a very rough surface texture with an almost sand

paper-like appearance. In mild cases, however, the surface will have normal smoothness with only an occasional grit particle protruding. Since gloss is not measurably reduced by such low levels of grit it becomes a subjective decision as to just how much grit is tolerable without unduly compromising appearance. Lower gloss coatings show similar behavior except that the grit is less apparent to the observer and therefore slightly higher levels may be allowable. For applications where appearance is not of major concern, other criteria will determine the acceptable grit level, for example, viscosity or mechanical strength. In such cases much higher levels of grit are usually permissible and other methods of assessing grit may be more useful.

In the present invention there is a net repulsive potential barrier height between the latex particles such that they themselves have a high degree of mutual stability, yet the repulsive potential barrier height between latex particles and inorganic material particles is sufficiently low such that there is a practically useful rate of accretion of latex particles on the inorganic material particles. The repulsive potential barrier between inorganic material particles themselves needs to be maintained only to a degree adequate such that they can be at least temporarily deagglomerated under the shearing forces during the mixing of the latex and inorganic material particles. In general, for particles stabilized by surface charges, the ordering of relative colloidal stability of the various particle pairs in the absence of shearing forces will be as follows: (latex-latex) is greater than (latex-inorganic material) which in turn is greater than (inorganic material-inorganic material). In general, the repulsive potentials between particles, unlike as well as like, will depend on surface potential or charge - varying to a first approximation as the product of the surface potentials on the two particles, the particle diameters, dielectric constant and ionic strength of the medium, and on the attractive force constant between the particles, e.g., the Hamaker constants.

In the first presently preferred embodiment of the process of the present invention the polymeric latex particles in the aqueous medium have a surface charge density or surface potential which is greater in absolute value than the surface charge density or surface potential of the inorganic material particles in

the aqueous medium.

It is understood that both the absolute values of the surface potentials and the magnitude of the difference in surface potentials are related to the force driving the adsorption, and in particular the magnitude of the electrical repulsion forces opposing adsorption.

An alternative way to stabilize colloidal particles against uncontrolled aggregation is to provide a surface layer or sheath of water soluble polymer around the colloidal particle, the chains of which polymer extend into the aqueous phase. This provides a steric barrier between the particles and between such a particle and other surfaces. A variety of water soluble polymers are suitable, e.g., polyacrylamide, polyvinyl alcohol, polyethylene oxide, water soluble polymers derived from cellulose. The water soluble polymers may be suitably attached to the particle surfaces by several means, among them by chemical grafting, such as through polymerizable unsaturated groups linked to the water soluble polymer, as well as by physical adsorption, often enhanced by the presence of a hydrophobic group attached to the water soluble polymer. The hydrophobic group may be simply a hydrocarbon chain or a water insoluble block polymer attached to the water soluble portion of the polymer. Steric stabilization has been thoroughly described by a number of authors, e.g., D.H. Napper, Polymeric Stabilization of Colloidal Dispersions, Academic Press, 1983; E.D. Goddard and B. Vincent, Polymer Adsorption and Dispersion Stability, ACS Symposium Series 240, 1984. Partial to thorough aggregation of sterically stabilized particles may be accomplished by reducing the solvency of the medium for the attached polymer chains, e.g., by variations in temperature, pressure, or composition of the liquid medium as described by Napper, 1983, chapter 5. For instance, a dispersion sterically stabilized with polyethylene oxide chains can be destabilized by the addition of salt or a water miscible non-solvent for the polymer.

Thus, as in the case of charge-stabilized particles, relative interparticle repulsive forces may be adjusted to permit controlled adsorption of, for example, latex particles onto a sterically stabilized polymeric particle surface. Hence, the present invention provides a process for preparing an aqueous dispersion of

composite particles, the process comprising suspending inorganic material particles in an aqueous medium. In this aspect, the process further includes suspending the polymeric latex particles in the aqueous medium, the polymeric particles being stabilized against homocoagulation by polymeric steric stabilization, the surface potential of one of either of the polymeric latex particles or the inorganic material particles in the aqueous medium being greater in absolute value than the surface potential of the other of the polymeric latex particles and the inorganic material particles. Also included is mixing the aqueous medium containing the inorganic material particles and the polymeric latex particles, the polymeric latex particles adsorbing onto the inorganic material particles to provide the composite particles.

In the case of particles stabilized by surface charge, an approximate measure of, and often useful guide to, the surface potential of particles in an aqueous medium is the particles' zeta potential. However, it should be noted that there may be a significant difference between the measured zeta potential and the potential at the true inorganic material particle surface when dispersants, surfactants, or other materials, such as cellulosic thickeners or protective colloids, are adsorbed onto the surface of the inorganic material particles.

The measurement of zeta potentials is discussed in detail in R.J. Hunter, Zeta Potential in Colloid Science (Academic Press 1981). Although a variety of techniques have been used for determining zeta potentials, the most common method for colloidal suspensions of either polymeric latex particles or dispersed inorganic pigment particles is electrophoresis, in which the movement of individual particles under the influence of an external electric field is observed, either directly, by a light microscope, or indirectly. The particle velocities or mobilities measured are then used to calculate the zeta potential. As measurements must be made at low concentrations (for example, at 0.1% w/w or less), samples often must be substantially diluted with an appropriate diluent, such as a standard reference solution, or an aliquot of the sample's own continuous phase obtained by filtration, centrifugation, or another method.

In the first preferred embodiment of the present process it is preferred that the zeta potential of the polymeric latex particles in the aqueous medium be

greater in absolute value (that is, more negative) than the zeta potential of the inorganic material particles in the aqueous medium. Preferably, the absolute value of the zeta potential of the polymeric latex particles is at least about 20 mv and more preferably at least about 40 mv, while the absolute value of the zeta potential of the inorganic material particles is at least about 5 mv and more preferably at least about 20 mv.

It is preferable that the surface potential of the polymeric latex be more negative than about -20 mV (measured as zeta potential) otherwise the polymeric latex particles themselves will tend to lack adequate stability despite the fact that they may nonetheless be attracted to and adsorb on an inorganic material particle. It is even more preferable in this regard that the surface potential be more negative than about -40 mV. On the other hand, it is preferred that the surface potential of the polymeric latex be not more negative than about -150 mV, otherwise the forces of electrostatic repulsion between the polymeric latex particle and a negatively charged inorganic material particle may be so strong as to preclude adsorption. Thus it is more preferred that the potential of the polymeric latex particles in a given practical circumstance be within these general ranges as determined by the rational empirical experimental procedure described above in the determination of surface saturation adsorption.

It is preferable that the surface potential of the inorganic material particle be more negative than about -5 mV, and even more preferable that it be more negative than about -20 mV. In any event it should not be more negative than about -70 mV, otherwise the repulsive forces between the inorganic particle and the emulsion polymer particle will be so great as to preclude adsorption for all practical purposes. Again, the optimum surface potentials are best established by the empirical procedure for the desired combination of inorganic particles and polymeric latex particles.

The surface potential and the zeta potential of a particle suspended in an aqueous medium can often be adjusted by changing the characteristics of the aqueous medium. For example, many inorganic particles have acidic and/or basic functional groups at their surfaces, or can be treated to provide such groups at the particles' surfaces, such as by adsorption of anionic pigment dispersants

and/or anionic surfactants, and the surface potential of these particles can be adjusted by varying the pH of the aqueous medium. Similarly, polymeric latex particles can be synthesized with acidic and/or basic functional groups at their surfaces, and the surface charge density of these particles can also be adjusted by varying the pH of the aqueous medium. In case of synthetic polymeric latex particles, the absolute value of the surface charge density can also be controlled by adjusting the density of surface acid and/or base groups through selection of polymer composition and polymerization process variables. An emulsion polymerization process which provides a preferential distribution of acid functionality for the particles, such as proximate the surface of the particles, can be used to prepare the polymeric latex particles.

The zeta potential of commercial grades of some types of inorganic material varies inversely with pH, such as from about 50 mv at a pH of about 3.5 to about -30 mv at a pH of about 11 (titanium dioxide). The zeta potential of many types of inorganic material particles is negative in a basic aqueous medium. Preferably, the zeta potential of the inorganic material used in the process of the present invention is negative, with a zeta potential from about -5 mv to -70 mv being preferred, a zeta potential from about -10 mv to -65 mv being more preferred, and a zeta potential from about -20 mv to -60 mv being especially preferred.

The zeta potential of the polymeric latex particles used in the first presently preferred embodiment of the process of this invention is more negative than the zeta potential of the inorganic material particles, and preferably is from about -20 mv to -120 mv, more preferably from about -40 mv to -110 mv.

The strength with which the polymeric latex particles are adsorbed onto the inorganic material particles reflects a balance between the material attraction forces, an approximate measure of which is the product of the respective Hamaker constants for the two types of particles, and electrical repulsive forces, an approximate measure of which is the product of the zeta potentials for the two types of particles. The geometric mean of the Hamaker constants for inorganic material and many types of synthetic polymer latexes in commercial use is estimated to be about  $1$  to  $3 \times 10^{-13}$  erg, but is dependent on the grade of inorganic material and polymer composition. On the other hand, the product of

the zeta potentials depends directly on the zeta potential of the polymeric latex particles (and the inorganic material particles), which can be adjusted by varying pH, polymer composition, polymerization process variables, and the like. In the first embodiment of the present process of the invention, the product of the zeta potentials preferably is from about 100 mv<sup>2</sup> to 8400 mv<sup>2</sup>.

Serum pH can have large effects on the surface potential of colloidal particles and accordingly can be used for purposes of adjustment as long as pH requirements are not fixed by other performance requirements of the coating or other aqueous formulation. For instance, metal container corrosion and rusting of ferrous substrates can occur if a coating formulation pH is too low, for example, less than about 7-8, and thus one could not access lower pH for the purpose of preparation of the colloidal microcomposites of the invention although, of course, pH can often be readjusted upward following their preparation at lower pH. It is well known that lower pH will tend to make the surface potential of particles more positive, and vice versa. The entire accessible pH scale is useful in the practice of this invention although it is preferred for reasons of excessive particle solubility, corrosion both to substrates and to the skin, and the like to restrict the range to approximately 2 to 12 and more preferably in the range of from about 4 to about 10. Numerous examples of the effect of pH on zeta potential both for inorganic and organic particles are found in texts on colloid chemistry such as R.J. Hunter, Zeta Potential in Colloid Science, Academic Press, 1981.

Another variable in controlling the adsorption process can be whether the inorganic particles have been subjected to prior surface treatment processes. For example, titanium dioxide is available with various types of prior surface treatments which provide surface coatings of alumina or silica or mixtures of both, the treated inorganic material particles each exhibiting differing adsorption characteristics, as discussed in A. Brisson et al., J. Coatings Tech. 63 59-65 (1991).

The ionic content of the serum can affect the particle adsorption process in several ways. Increased serum ionic content, for example, as expressed in terms of ionic strength, reduces the repulsive force between the charged particles thereby promoting the adsorption. Also, for a given organic or inorganic

colloidal particle, there may be a specific adsorption of certain ions, and the surface potential of the particle will be raised or lowered according to the sign of charge of the ion. In general, however, one usually desires to minimize the electrolyte content of aqueous polymeric latex formulations because of deleterious effects on water resistance of the dried films or coatings, and it is more advantageous to adjust surface potentials of the emulsion and inorganic particles by more selective additives such as the dispersants such as those of the polyelectrolyte type and surface active agents heretofore noted. However, in the case of an ion which may specifically and efficiently adsorb on a particle its use may be advantageous. For example, multivalent cations such as  $Al^{3+}$  are useful at low levels, for example, less than about one percent based on the weight of the inorganic particle, in reducing the surface charge of inorganic material particles, without resorting to pH reduction alone. Additional examples of the effect of ionic content on surface potential are described in standard texts such as Hunter's Zeta Potential in Colloid Science.

The adsorption process of the present invention is dependent on the particle sizes of the polymeric latex particles and the inorganic material particles to be dispersed therewith, as well as the amount of the polymeric latex and inorganic material particles in the aqueous adsorption medium. An important variable in the process is whether the amount of the selected polymeric latex used to disperse the inorganic material particles is present at a concentration which is sufficient to adsorb onto and saturate the entire surface of the inorganic material particle surface. It is believed that the empirical saturation level observed depends primarily on particle size, and that other factors such as surface charge, polymeric latex glass transition temperature, and the like, have little effect.

Applying geometric principles, the saturation concentration of one spherical particle on the surface of another spherical particle can be calculated from the relative particle sizes of the polymeric latex particle and the inorganic material particle, provided that certain assumptions are made, such as, for example, that the polymeric latex particles are spherical, that they do not deform upon adsorption, and that they are able to totally encapsulate the entire surface of the inorganic material particle. The minimum amount or number of a specific type



of spherical polymeric latex particles which can saturate the surface of a specific type of spherical inorganic material particle is determined empirically and is referred to herein as the "saturation level" of the polymeric latex particle on that inorganic material particle. The empirically determined saturation level has been found to be about one-third to one-half the calculated saturation level for instances where such calculations are possible, the difference being believed attributable to geometric and other factors. The saturation level is useful as a guide for evaluating the progress or extent of the controlled adsorption process of the invention. It is preferred that the process of the present invention be carried out at or above the saturation level, in order to obtain optimum performance properties in fully formulated products prepared using the process.

In practice, commercially available particles, especially inorganic material particles such as pigments and fillers are rarely uniform in size and spherical in shape, and in fact vary widely in size and shape, even within a given material. The surfaces of the particles may also vary from point to point in colloidal characteristics such as in local surface charge and potential. Furthermore, a polymeric latex particle once adsorbed may not have adequate lateral mobility that permits rearrangement in the presence of other adsorbed particles to achieve close packing of the polymeric latex particles on the surface of the inorganic material particle. In addition, since the adsorbed latex particles generally will bear significant repulsive surface potential, there will be tendency for lateral repulsive forces between them which may also be sufficient to hinder close packing.

Thus, in the practice of this invention the determination and establishment of the surface saturation condition is conducted in an empirical but rational manner through experimental measurements of adsorption, increasing the concentration and/or total amount of polymeric latex offered to the inorganic material particles until the amount of polymeric latex adsorbed per unit of inorganic particle approaches a plateau value. This plateau level of adsorption is referred to as the saturation level of adsorption. The saturation level is a guide for utility of the adsorption conditions for practice of the invention in as much as adsorption levels much less than those of saturation tend to result in

microcomposite particles that have inadequate stability relative to each other and will tend to undergo further and more macroscopic aggregation resulting in grit in end use systems such as coatings and films that will detract not only from appearance but from other desirable optical, physical, and resistance properties.

In preparing formulations possessing desirable performance properties it may be desirable for the polymeric latex used in the controlled adsorption process of the invention to also function as the polymeric binder for the coating or film. In order for a polymeric latex to function as a binder it will typically be required to be present in the coating or film formulation in an amount greater than its saturation level, especially in formulations requiring a low pigment volume concentration. Therefore, when in one embodiment of the process of this invention the selected polymeric latex is to be used as both a dispersant for the inorganic material particles and as a binder for the coating or film, the proportion of the polymeric latex which is adsorbed on the inorganic material particles will be related to the desired pigment volume concentration ("PVC") of the coating or film.

The absolute percentage of the total amount of the polymeric latex used in the process which actually becomes adsorbed onto the inorganic material particles is not, therefore, in this embodiment of the process of the present invention, a meaningful expression of the efficiency of the controlled adsorption process of the invention, without reference to the saturation level of the polymeric latex relative to the inorganic material particles onto which it is to be adsorbed. For example, at coating pigment volume concentrations at which the polymeric latex is present at concentrations below the saturation level (i.e. high PVC), the percent of polymeric latex adsorbed onto the inorganic material particles may approach 100%, but this does not indicate whether the adsorption process will be effective in providing stability to the composite particle or improved performance properties for the coating or film.

The advantages of the process of the invention may not be achieved even at 100% adsorption if an insufficient amount of the polymeric latex were available for dispersing the inorganic material particles in a controlled manner. Similarly, in coating or film formulation where the polymeric latex also functions as the

binder and where the pigment volume concentration of the coating or film reflects a concentration of polymeric latex at or above the saturation level (i.e. low PVC), the absolute percentage of the polymeric latex which is adsorbed onto the inorganic material particles may be much lower than the absolute percentage of polymeric latex adsorbed on the same inorganic material particles at concentrations below the saturation level, but the adsorption process is effective and controlled. This result is primarily due to the fact that because there is more polymeric latex present than that which can possibly adsorb onto the inorganic material particles (at or above the saturation level), the advantages of the controlled adsorption process may be achieved even though not all the polymeric latex present is functioning in the adsorption process. Accordingly, when evaluating the effectiveness of the process of the invention it is more important to determine the extent of the adsorption of the polymeric latex onto the inorganic material particles relative to the saturation concentration of the polymeric latex than to determine the absolute percentage of the polymeric latex which has adsorbed onto the inorganic material particles.

With regard to the average particle size or diameter of the polymeric latex particles and the inorganic material particles employed in the present process, it is generally preferred that the polymeric latex particles have an average diameter of from about 20 nm to about four times that of the inorganic material particles. However, the optimum relative particle sizes are strongly dependent on the rigidity of the polymeric latex particles, as measured, for example, by their glass transition temperature, and the pigment volume concentration of the coating or product formed from the composition including the composite particles. The average particle size or diameter of the polymeric latex particles can range from about 20 nm to 20,000 nm, as the average particle size of the inorganic particles can range from about 100 nm to 10,000 nm.

The concentration of the inorganic material particles (and any other pigments which may be present in the composition) in a coating formulation is expressed in terms of the pigment volume concentration of the formulation. The pigment volume concentration (hereinafter referred to as the "PVC") of a formulation is defined as the volume amount of inorganic particles, including inorganic

material and other pigment particles as well as extender particles, present in the formulation, divided by the sum of the volume amount of such inorganic particles plus polymeric latex particle solids in the formulation. The overall concentration of pigment particles, extender particles and emulsion polymer particles in a formulation is typically expressed in terms of a percent volume solids for the formulation. The percent volume solids is an expression of the extent of the dilution of the solids in a liquid vehicle, such as water.

If the selected polymeric latex is employed at a concentration equal or greater than the saturation level for the selected inorganic material particle, the extent of adsorption of the polymeric latex on the surface of the inorganic material particle is maximized, and that under such circumstances the viscosity of the dispersed formulation (referred to hereinafter as the "grind" and "grind viscosity", respectively) is effectively minimized. The minimization of the grind viscosity is an expression of the effectiveness of the controlled adsorption process for stabilizing the inorganic material particles. Minimizing the grind viscosity is of commercial importance for transporting highly concentrated dispersions of the inorganic material particles prior to formulating the dispersion into a coating or film. Consequently, the process of the present invention advantageously provides highly concentrated inorganic material slurries with minimized viscosities.

Further, through the selection of the polymeric latex composition the adsorption of the polymeric latex particles on the surface of the inorganic material particle can occur substantially upon the intimate mixing or grinding of the polymer latex with the inorganic material particles, depending upon the selection of process conditions. The ability to effect substantially immediate adsorption is an important aspect of the present invention as it minimizes any delay between the preparation of the dispersed inorganic material dispersion and its transportation or use in preparing the final formulation.

It is desired that conditions be selected so that the rate of formation of the composite particles be significantly greater than the rates of competing processes, such as the formation of aggregates of inorganic material particles (i.e. homocoagulation processes), while at the same time the formation of aggregates

including multiple inorganic material particles and polymeric latex particles are substantially avoided. Thus, in terms of interaction strengths, the homoparticle interactions should be repulsive enough to prevent significant homocoagulation of the inorganic material particles for a long enough period to permit formation of the composite particles, while heteroparticle interactions should be attractive enough to drive the formation of composite particles before significant homocoagulation occurs, but not so great so that rapid heteroparticle interaction results in the formation of significant amounts of aggregated material including multiple inorganic material particles ("grit"). The extent of grit formation can be assessed empirically by making a draw-down of the fully formulated composition including the composite particles and noting the appearance of granular or irregular texture. Thus, grit formation is more readily apparent, and more undesirable, in gloss and semi-gloss coating compositions, than in flat paints, for example. Variables which influence the relative magnitudes of the homoparticle interaction and the heteroparticle interaction include Hamaker constants, particle surface charge, the presence and nature of dispersants or surfactants adsorbed on the surface of the inorganic material particles, the pH and ionic strength of the aqueous medium, as well as adsorption reaction conditions such as particle concentrations, temperature, and agitation.

The polymeric latexes used in the practice of the process of the present invention can have monomer compositions and particle sizes typical of polymeric latex binders prepared by standard emulsion polymerization techniques known in the art. If it is otherwise desirable to employ conventional levels of a polyelectrolyte dispersant in a pigment dispersion, it may be possible to employ an irreversibly adsorbing polymeric latex to adsorb to the inorganic material particles. Irreversibly adsorbing polymeric latex particles can be prepared by emulsion polymerization processes by selection of process variables and the monomer composition.

In one class of embodiments of the process of the present invention, the polymeric latex particles serve as binder for the product formed by the fully formulated aqueous composition. In this case the effective glass transition temperature of the adsorbed polymeric particles is preferably less than about

60°C, assuming the fully formulated composition is intended for use at room temperature, and film formation must consequently take place at room temperature.

In one aspect of this class of embodiments, the polymeric latex particles are selected such that they can be used to disperse the inorganic material particles in the absence of a polyelectrolyte dispersant and also serve as binder for the product. In another aspect of this embodiment, the polymeric latex particles are selected such that they can be employed to displace a polyelectrolyte pigment dispersant from the surface of the inorganic material particles. When the polymeric latex particles are used to displace a pigment dispersant, it is preferable that the factors relating to adsorption, such as the polymeric latex surface potential, are chosen so that polymeric latex particles bind irreversibly to the inorganic material particles.

In another class of embodiments of the process of the present invention, the polymeric latex particles do not themselves provide a binder for the product formed by the fully formulated aqueous composition. Because they are not required to flow and form a film, the particles can be more rigid than those employed to provide a binder. Thus, the polymeric particles can have a higher effective glass transition temperature than polymeric particles employed to serve as binder, and can include rigidifying levels of crosslinking. In this case the polymeric latex can also be prepared by standard emulsion polymerization techniques, but typically will not possess the requisite low glass transition temperature suitable for use as a film-forming binder, for example, for paint to be dried at ambient room temperature, or adhesive material. In this case, the effective glass transition temperature of the polymeric latex particles is preferably at least about 50°C.

The polymeric latex particles used in these embodiments are preferably selected based on an ability to adsorb rapidly and irreversibly onto the inorganic material particles. Such particles are not displaced from the surface of the inorganic material particles upon addition of a second variety of polymeric latex having a monomer composition and physical properties which differ from that of the initial polymeric latex.

This aspect of the invention advantageously provides enhanced flexibility in formulation. For example, the second variety of polymeric latex particles can be polymeric latex which has a monomer composition and physical properties which have been optimized for use as a binder for a specific coating application. Some of these optimized properties may not be consistent with use of this specific polymeric latex as a pigment dispersant in the process of the present invention.

In one subclass of these embodiments, the polymeric latex particles of the first variety are used initially to disperse the inorganic material particles, and the second variety of polymeric latex particles, the binder-forming particles, are subsequently mixed with the dispersed inorganic material particles. In another subclass of these embodiments, dispersion can be otherwise effected, as with a polyelectrolyte pigment dispersant, with a mixture of irreversibly adsorbing polymeric latex particles and binder latex particles being subsequently mixed with the dispersed inorganic material particles, the irreversibly adsorbing polymeric latex particles in the presence of the pigment dispersant and advantageously spacing the inorganic material particles in the product of the formulated composition to give improved application properties, while the binder latex particles provide a continuous film otherwise optimized for the application.

Irreversibly adsorbing polymeric latex particles useful in the process of this invention may be prepared by several alternative processes. In one such process, emulsion polymerization process variables are controlled to provide a preferred distribution of acid functionality for the polymer latex particles. In particular, processes which provide carboxylate functionality preferentially at the surface of the polymeric latex particles are preferred.

In another process for preparing irreversibly adsorbing polymeric latex particles, the monomer mixture from which the polymeric latex is polymerized includes at least one dihydrogen phosphate ester of an alcohol in which the alcohol contains a polymerizable vinyl or olefinic group; examples include allyl phosphate, alkyl cellosolve phosphate, hydroxyethyl methacrylate phosphate, the mono- or diphosphate of bis(hydroxyethyl) fumarate or itaconate, etc. In particular, polymeric latex particles polymerized from monomer mixtures

including the dihydrogen phosphate ester of 2-hydroxyethyl methacrylate are preferred.

In yet another process for preparing irreversibly adsorbing polymeric latex particles, the monomer mixture from which the polymer latex is polymerized includes at least one ethylenically unsaturated, polymerizable, dicarboxylic acid. In particular, polymeric particles polymerized from monomer mixtures including itaconic acid are preferred.

In general it is believed that reducing the effective glass transition temperature of the polymeric latex (for example, by changing the monomer composition) increases the tendency to adsorb irreversibly, as does increasing the level of acid- functional monomers or the level of phosphate ester-functional monomers or itaconic acid in the composition.

Thus, in a preferred embodiment, the present invention provides aqueous dispersions of composite particles, as well as coating compositions and pigment slurries including such composite particles, wherein the composite particles each comprise a plurality of polymeric latex particles adsorbed to an inorganic material particle, the polymeric latex particles including dihydrogen phosphate ester functional groups. These dihydrogen phosphate ester functional groups are believed to result from the polymeric latex particles being polymerized from monomer including at least one polymerizable dihydrogen phosphate-functional monomer. The polymerizable dihydrogen phosphate-functional monomer can be selected from the dihydrogen phosphate esters of an alcohol, the alcohol including a polymerizable group selected from polymerizable vinyl groups and polymerizable non-vinyl olefinic groups. Preferably, the polymerizable dihydrogen phosphate- functional monomer is selected from the dihydrogen phosphate monoester of 2-hydroxyethyl methacrylate, and mixtures of the dihydrogen phosphate monoester of 2-hydroxyethyl methacrylate and the phosphoric acid diester of 2-hydroxyethyl methacrylate. Similarly, the present invention provides aqueous dispersions of composite particles, and coating compositions and pigment slurries including such composite particles, in which the composite particles each comprising a plurality of polymeric latex particles adsorbed to a inorganic material particle, the



polymeric latex particles including polymerized residues of itaconic acid.

The polymeric latex used in the present invention can be prepared by any technique known in the art, such as suspension polymerization, interfacial polymerization, or emulsion polymerization. Emulsion polymerization techniques for preparing aqueous dispersions of latex polymer particles from ethylenically unsaturated monomers are well known in the polymer arts, and any conventional emulsion technique can be used, such as single and multiple shot batch processes, and continuous processes. If desired, a monomer mixture can be prepared and added gradually to the polymerization vessel. The monomer composition within the polymerization vessel can be varied during the course of the polymerization, such as by altering the composition of the monomer being fed into the vessel. Both single and multiple stage polymerization techniques can be used. The latex polymer particles can be prepared using a seed polymer emulsion to control the number of particles produced by the emulsion polymerization as is known in the art. The particle size of the latex polymer particles can be controlled by adjusting the initial surfactant charge as is known in the art. The preparation of polymeric latexes is discussed generally in D.C. Blackley, Emulsion Polymerization (Wiley, New York, 1975). The preparation of acrylic polymeric latexes is described in, for example, Emulsion Polymerization of Acrylic Polymers, Bulletin, Rohm and Haas Company, Philadelphia.

A polymerization initiator can be used in carrying out the polymerization of the polymeric latex particles. Examples of polymerization initiators which can be employed include polymerization initiators which thermally decompose at the polymerization temperature to generate free radicals. Examples include both water-soluble and water-insoluble species. Examples of free radical-generating initiators which can be used include persulfates, such as ammonium or alkali metal (potassium, sodium or lithium) persulfate; azo compounds such as 2,2'-azo-bis(iso-butyronitrile), 2,2'-azo-bis(2,4-dimethylvaleronitrile), and 1-t-butyl-azocyanocyclohexane; hydroperoxides such as t-butyl hydroperoxide and cumene hydroperoxide; peroxides such as benzoyl peroxide, caprylyl peroxide, di-t-butyl peroxide, ethyl 3,3'-di(t-butylperoxy) butyrate, ethyl

3,3'-di(t-amylperoxy) butyrate, t-amylperoxy-2-ethyl hexanoate, and t-butylperoxy pivalate; peresters such as t-butyl peracetate, t-butyl perphthalate, and t-butyl perbenzoate; as well as percarbonates, such as di(1-cyano-1-methylethyl)peroxy dicarbonate; perphosphates, and the like.

Polymerization initiators can be used alone or as the oxidizing component of a redox system, which also includes a reducing component such as ascorbic acid, malic acid, glycolic acid, oxalic acid, lactic acid, thioglycolic acid, or an alkali metal sulfite, more specifically a hydrosulfite, hyposulfite or metabisulfite, such as sodium hydrosulfite, potassium hyposulfite and potassium metabisulfite, or sodium formaldehyde sulfoxylate. The reducing component is frequently referred to as an accelerator or a catalyst activator.

The initiator and accelerator, commonly referred to as catalyst, catalyst system or redox system, can be used in proportion from about 0.001% to 5% each, based on the weight of monomers to be copolymerized. Promoters such as chloride and sulfate salts of cobalt, iron, nickel or copper can be used in small amounts. Examples of redox catalyst systems include tert-butyl hydroperoxide/sodium formaldehyde sulfoxylate/Fe(II), and ammonium persulfate/sodium bisulfite/sodium hydrosulfite/Fe(II). The polymerization temperature can be from room temperature to about 90°C, and can be optimized for the catalyst system employed, as is conventional.

Chain transfer agents can be used to control polymer molecular weight, if desired. Examples of chain transfer agents include mercaptans, polymercaptans and polyhalogen compounds. Examples of chain transfer agents which may be used include alkyl mercaptans such as ethyl mercaptan, n-propyl mercaptan, n-butyl mercaptan, isobutyl mercaptan, t-butyl mercaptan, n-amyl mercaptan, isoamyl mercaptan, t-amyl mercaptan, n-hexyl mercaptan, cyclohexyl mercaptan, n-octyl mercaptan, n-decyl mercaptan, n-dodecyl mercaptan; mercapto carboxylic acids and their esters, such as methylmercaptoproionate and 3-mercaptopropionic acid; alcohols such as isopropanol, isobutanol, lauryl alcohol and t-octyl alcohol; halogenated compounds such as carbon tetrachloride, tetrachloroethylene, and trichloro-bromoethane. Generally from 0 to 10% by weight, based on the weight of the monomer mixture, can be used. The polymer

molecular weight can be controlled by other techniques known in the art, such as selecting the ratio of initiator to monomer.

Catalyst and/or chain transfer agent can be dissolved or dispersed in separate or the same fluid medium and gradually added to the polymerization vessel. Monomer, either neat or dissolved or dispersed in a fluid medium, can be added simultaneously with the catalyst and/or the chain transfer agent. Amounts of initiator or catalyst can be added to the polymerization mixture to "chase" residual monomer after polymerization has been substantially completed to polymerize the residual monomer as is well known in the polymerization arts.

Aggregation of polymeric latex particles is typically discouraged by including a stabilizing surfactant in the polymerization mix. In general, the growing latex particles are stabilized during emulsion polymerization by one or more surfactants such as an anionic or nonionic surfactant, or a mixture thereof, as is well known in the polymerization art. Many examples of surfactants suitable for emulsion polymerization are given in McCutcheon's Detergents and Emulsifiers (MC Publishing Co., Glen Rock, NJ), published annually. Other types of stabilizing agents, such as protective colloids, can also be used. However, it is preferred that the amount and type of stabilizing surfactant or other type of stabilizing agent employed during the polymerization reaction be selected so that residual stabilizing agent in the aqueous product of the polymerization reaction does not significantly interfere with the subsequent adsorption of the polymeric latex to the inorganic material particle. Further, charged initiator fragments and copolymerized monomer bearing charged functional groups such as copolymerized acid-functional monomers are known to contribute to the stability of the resulting polymeric latex particles. It is important to note that stabilizing surfactants, copolymerized acidic monomers, residual initiator fragments, and the like, which tend to contribute to stability of the polymeric latex particles with respect to aggregation, or homocoagulation, may also tend to stabilize the polymeric latex particles with respect to heterocoagulation in general, and composite particle formation in particular. Thus adjusting polymerization conditions to provide a desired level of residual initiator fragments and surface acid may be very important in providing polymeric latex

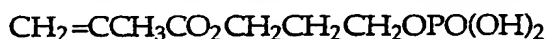
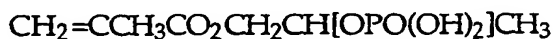
particles for use in the controlled adsorption process of the present invention.

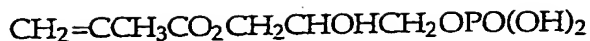
The polymeric latexes useful in the process of the present invention can be prepared from a wide range of polymerizable monomers, such as, for example, monoethylenically unsaturated monomers, including alpha, beta-monoethylenically unsaturated monomers such as alkyl acrylates and methacrylates. By "acrylic polymeric latex" is meant a polymeric latex polymerized from monomers comprising substantially polymerizable monomers including the acryl group ( $-\text{COCH}=\text{CH}_2$ ) or methacryl ( $-\text{COC}(\text{CH}_3)=\text{CH}_2$ ) group, and specifically greater than about 80 weight percent (meth)acrylic monomers, based on the total monomer weight. Mixtures of polymeric latexes can also be used.

Examples of polymeric latexes which can be employed in the process of the present invention include those polymerized from ethylenically unsaturated monomers, such as alpha, beta- ethylenically unsaturated monomers, including styrene, butadiene, alpha-methylstyrene, vinyltoluene, vinylnaphthalene, ethylene, vinyl acetate, vinyl versatate, vinyl chloride, vinylidene chloride, acrylonitrile, methacrylonitrile, (meth)acrylamide, various ( $\text{C}_1$ - $\text{C}_{20}$ )alkyl esters of (meth)acrylic acid; for example, methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, cyclohexyl (meth)acrylate, n-octyl (meth)acrylate, n-decyl (meth)acrylate, n-dodecyl (meth)acrylate, tetradecyl (meth)acrylate, n-amyl (meth)acrylate, neopentyl (meth)acrylate, cyclopentyl (meth)acrylate, lauryl (meth)acrylate, oleyl (meth)acrylate, palmityl (meth)acrylate, and stearyl (meth)acrylate; other (meth)acrylates such as isobornyl (meth)acrylate, benzyl (meth)acrylate, phenyl (meth)acrylate, 2-bromoethyl (meth)acrylate, 2-phenylethyl (meth)acrylate, and 1-naphthyl (meth)acrylate; alkoxyalkyl (meth)acrylate such as ethoxyethyl (meth)acrylate; mono-, di- and trialkyl esters of ethylenically unsaturated di- and tricarboxylic acids and anhydrides, such as ethyl maleate, dimethyl fumarate, trimethyl aconitate, and ethyl methyl itaconate. As used in the present specification and claims, "(meth)acrylate" denotes both "acrylate" and "methacrylate" and "(meth)acrylic denotes both "methacrylic" and "acrylic."

The ethylenically unsaturated monomer can also include at least one multi-ethylenically unsaturated monomer effective to raise the molecular weight and crosslink the polymer. Examples of multi-ethylenically unsaturated monomers that can be used include allyl (meth)acrylate, tripropylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, ethylene glycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,3-butylene glycol (meth)acrylate, polyalkylene glycol di(meth)acrylate, diallyl phthalate, trimethylolpropane tri(meth)acrylate, divinylbenzene, divinyltoluene, trivinylbenzene, and divinyl naphthalene.

In addition to those monomers which are "functional" in the sense of including one or more polymerizable ethylenically unsaturated groups, monomers which also include one or more additional functional groups can be used in preparing the polymeric latexes used in the process of this invention. An important class of these functional monomers is that made up of the those polymerizable ethylenically unsaturated monomers having acidic functional groups. Examples of these include acrylic acid, methacrylic acid, itaconic acid, beta-acryloxypropionic acid and higher monoacidic oligomers of acrylic acid, ethacrylic acid, alpha-chloroacetic acid, alpha-vinylacrylic acid, crotonic acid, alpha-phenylacrylic acid, cinnamic acid, chlorocinnamic acid, beta-styrylacrylic acid, itaconic acid, maleic acid, dihydrogen phosphate esters of an alcohol in which the alcohol also contains a polymerizable vinyl or olefinic group, such as allyl phosphate, allyl Cellusolve phosphate, mono- or diphosphate of bis(hydroxy-ethyl) fumarate or itaconate, derivatives of (meth)acrylic acid esters, such as, for example, phosphates of hydroxyalkyl(meth)acrylates including 2-hydroxyethyl (meth)acrylate, such as Kayamer (trademark of Nihon Kayaku Co., Ltd.) PM-1, PM-2, PA-1, and PA-2 monomers, 3-hydroxypropyl (meth)acrylates, and the like. Examples of dihydrogen phosphate ester derivatives which can be employed include vinylbenzyl phosphates, and:





Thus, the present invention also provides aqueous dispersions of composite particles, as well as coating compositions and pigment slurries including such composite particles, in which the composite particles include polymeric latex particles polymerized from monomer including at least one polymerizable dihydrogen phosphate-functional monomer selected from the dihydrogen vinylbenzyl phosphates, and  $\text{CH}_2=\text{CCH}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{OPO(OH)}_2$ ,  $\text{CH}_2=\text{CCH}_3\text{CO}_2\text{CH}_2\text{CH}[\text{OPO(OH)}_2]\text{CH}_3$ ,  $\text{CH}_2=\text{CCH}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OPO(OH)}_2$ ; and  $\text{CH}_2=\text{CCH}_3\text{CO}_2\text{CH}_2\text{CHOHCH}_2\text{OPO(OH)}_2$ .

Small amounts of acid-functional copolymerizable monomer, such as methacrylic acid, acrylic acid, and/or itaconic acid, are typically included in preparing polymeric latexes to confer colloidal stability. As noted above, in one embodiment of the present invention, preparation of polymeric latex particles from monomer mixture including itaconic acid is preferred. In another presently preferred embodiment of the present invention, as noted above, the polymeric latex employed is polymerized from monomer mixture including at least one dihydrogen phosphate ester of an alcohol, the alcohol containing a polymerizable vinyl group or other polymerizable olefinic group, such as a dihydrogen phosphate derivative of a (meth)acrylic acid ester.

In the emulsion copolymerization of ethylenically unsaturated monomers including minor amounts (such as less than about ten percent by weight) of ethylenically unsaturated carboxylic acid-functional comonomers such as (meth)acrylic acid, the resulting polymeric acid groups may be buried inside the colloidal polymeric particles produced by the polymerization and consequently inaccessible to species dissolved in the aqueous phase, or the polymeric acid groups may be at or near the surface of the particles, or even present in the aqueous phase in the form of water-soluble polymer. In addition, some of the acid-functional monomer may remain unpolymerized. This residual monomer is usually to be found in the aqueous phase. Acid functionality which is at or near the surface of the particles (that is, proximate the surface of the polymeric latex particles) can be measured by potentiometric or conductometric titration

techniques.

For example, if the polymeric latex particles are treated with ion-exchange resin and then titrated conductometrically, the amount of carboxylic acid at or near the surface of the particles can be measured as described in H.J. Van den Hul and J. W. Vanderhoff, Electro. Chem. Interfac. Electrochem., **37** 161-182 (1972). High levels of surface carboxylic acid promote the adsorption process of this invention.

For the same mixture of monomers, the amount of surface carboxylic acid groups in the resulting polymeric latex particles depends on the specific emulsion polymerization employed. A number of factors can be important, including the particle size of the resulting polymeric latex, the pH of the polymerization medium, how the monomer is added to the polymerization reactor, and the choice of carboxylic acid monomer. For instance, if a mixture of 50 percent by weight butyl acrylate, 49 percent methyl methacrylate, and one percent methacrylic acid is gradually added to a polymerization reactor after the polymerization has been initiated, such as in a conventional gradual addition process, to give 200 nm polymer particles, titration indicates that about 25 percent of the total methacrylic acid is "surface acid," at or near the surface of the polymeric latex particles. If acrylic acid is substituted for methacrylic acid, the surface acid can increase. Similarly, if the process is altered so that all the monomer is added to the reactor, and the polymerization is then initiated, as is practical in a small-scale batch process, the surface acid can be found to be somewhat higher. In the present application, a process which preferentially provides acid functionality proximate the surface of the polymer latex particles is one which provides greater surface acid functionality than a conventional gradual addition process, or a conventional "single shot" batch process (such as a conventional process in which base is not added to the polymerization mix and the acidic functional groups consequently remain substantially nonionized through the polymerization process), as determined by potentiometric titration.

There are a number of ways known in the art for increasing the fraction of the acid that becomes surface acid. For example, if enough base is added during the polymerization to partially neutralize the carboxylic acid, the surface acid can be

increased measurably. However, higher levels of base can decrease surface acid. If the carboxylic acid monomer is added to the reactor in a nonuniform manner, the amount of surface acid can be increased. Examples of nonuniform carboxylic acid monomer additions that increase surface acid are described in K.L. Hoy, J. Coat. Tech., 51 27-41 (1979).

Other types of copolymerizable functional monomers can also be included, depending on the ultimate application for which the product produced by the process of the present invention is intended. For example, small amounts of adhesion-promoting copolymerizable monomers can also be included. Examples of other types of functional monomers include hydroxy-functional monomers such as 2-hydroxyethyl (meth)acrylate, amino-functional monomers such as dimethylaminoethyl (meth)acrylate, epoxy-functional monomers, such as glycidyl methacrylates and the like.

Examples of synthetic polymeric latexes which can be used include acrylic copolymer latexes, such as butyl acrylate/methyl methacrylate/acid and ethyl acrylate/methyl methacrylate/acid copolymer latexes; vinyl acetate homopolymer and copolymer latexes, including ethylene/vinyl acetate copolymer latexes, styrene/butadiene copolymer latexes, and the like.

By selecting the type and concentration of monomers having known glass transition temperatures and acid functionalities, polymeric latexes having properties useful in the process of the invention as well as being specifically suited as binders for the specific coating or film formulation application can be prepared.

The particle size and molecular weight of the polymeric latex can be selected by the choice of a particular polymerization process, as for example through the use of particular initiator and chain transfer systems, as is well known in the polymerization arts. The average particle size and the molecular weight of the polymeric latex are important with regard to both the adsorption onto the inorganic material particles, as well as with respect to the properties of the polymeric latex when it is employed as a binder in the the fully formulated aqueous composition including the composite particles.

Preferably, the polymeric latex used in the process of the present invention of



adsorbing onto and dispersing the inorganic material particles has an average particle diameter in the range of from approximately four times the average particle diameter of the inorganic material pigment particles down to about 20 nm. For example, if the inorganic material particle to be dispersed has an average particle size of about 200 nanometers, the polymeric latex particle should have an average particle size in the range of from about 20 to less than about 800 nanometers.

For example, polymeric latex is used in the process of the present invention for adsorbing onto and dispersing the titanium dioxide particles has an average particle diameter in the range of from approximately four times the average particle diameter of the titanium dioxide pigment particles down to about 20 nm, and more preferably from approximately equal to the average diameter of the titanium dioxide particles down to about one-quarter the average diameter of the titanium dioxide particles.

For example, if the titanium dioxide particle to be dispersed has an average particle size of about 200 nanometers, the polymeric latex particle should have an average particle size in the range of from about 20 to less than about 800 nanometers. When the polymeric latex particles are employed in the process of the invention at or above the natural saturation level relative to the titanium dioxide particle, polymeric latex of the same composition having relatively larger particle sizes, within the above range, are preferable to polymeric latex of the same composition having relatively smaller average particle diameters, within the above range, for maximizing the extent of adsorption onto the surface of the titanium dioxide particles. By "average particle size" or "average particle diameter" is meant an average determined experimentally by the quasielastic light scattering technique, such as provided, for example, by the Model BI-90 Particle Sizer, of Brookhaven Instruments Corp.

When the polymeric latex particles are employed in the process of the invention at or above the natural saturation level relative to the inorganic material particle, polymeric latex of the same composition having relatively larger particle sizes, within the above range, are preferable to polymeric latex of the same composition having relatively smaller average particle diameters,

within the above range, for maximizing the extent of adsorption onto the surface of the inorganic material particles. By "average particle size" or "average particle diameter" is meant an average determined experimentally by the quasielastic light scattering technique, such as provided, for example, by the Model BI-90 Particle Sizer, of Brookhaven Instruments Corp.

The selection of the relative surface charges of the polymeric latex particles and the inorganic material particles in the medium used for conducting the adsorption process is an important variable which effects both the extent of adsorption and the stability of the resulting dispersion of composite particles. It is preferred that the surface charge of the polymeric latex be of the same sign of charge as the sign of the surface charge of the inorganic material particle onto which the polymeric latex is to be adsorbed. More particularly, in aqueous formulations it is preferred that the polymeric latex and the inorganic material particle onto which it is to be adsorbed, both have a negative surface charge. Furthermore, it is preferred that the surface charge on the polymeric latex be more negatively charged than the surface charge on the inorganic material particle. It is especially preferred that the surface charge on the polymeric latex be at least about 30 millivolts more negatively charged than the surface charge on the inorganic material particle.

For example, in the case of the adsorption of a polymeric latex onto the surface of inorganic material particles, where the zeta potential of the inorganic material particles in the aqueous medium is about -50 mv, it is believed that minimum grit formation occurs, at the saturation level, when the zeta potential of the polymeric latex is more negative than -50 mv, preferably from about -50 mv to about -100 mv. The polymeric latex particles preferably have a surface charge of from about -40 mv to about -110 mv in order to adsorb onto, and form a stable dispersion with, the inorganic material particles, in those cases in which the inorganic material particles have a zeta potential from about -20 mv to -60 mv.

As in other aqueous systems including charged particles, the magnitude of the effective electrical repulsive forces depends on the dielectric strength and the ionic strength of the medium. As a practical matter, the dielectric strength will

be determined by the dielectric constant of water, because, while many aqueous coating compositions include small amounts of organic cosolvents for various purposes, such as encouraging coalescence and film formation by polymeric latex particles used as binder, these do not significantly vary the dielectric constant of the medium.

On the other hand, the ionic strength of the medium in coating compositions can vary over a significant range, and include contributions from a variety of simple ions and polyionic species. For example, coatings compositions typically range in pH from about 6 to 11 or more, a range of five orders of magnitude in the concentration of hydroxyl ion. While the strength of the repulsive forces between the polymeric latex particles and the inorganic material particles can be varied to some extent by adjusting the ionic strength of the aqueous medium through varying the pH and by addition of charged species, in general it is more desirable to vary the surface charge density as reflected by the zeta potential of the polymeric latex particles instead.

Varying the pH is of course likely to change the zeta potential of both the inorganic material particles and the polymeric latex particles directly. However, charged species added to adjust the ionic strength will also be present in the formulated coating composition, and the product formed by the coating composition, and the effect of the presence of the charged species on the formulated coating composition and the ultimate product must be carefully considered. Preferably, in most cases, no ionic species are added merely to adjust the ionic strength of the medium, and any desired adjustment in the magnitude of the electrical repulsive forces is effected in another manner.

Varying the pH is of course likely to change the zeta potential of both the titanium dioxide particles and the polymeric latex particles directly. However, charged species added to adjust the ionic strength will also be present in the formulated coating composition, and the product formed by the coating composition, and the effect of the presence of the charged species on the formulated coating composition and the ultimate product must be carefully considered. Preferably, in most cases, no ionic species are added merely to adjust the ionic strength of the medium, and any desired adjustment in the magnitude

of the electrical repulsive forces is effected in another manner. This is because added ionic species may have an undesirable effect on the properties of the product formed using the composition including the composite particles. For example, if ionic strength is increased by addition of a simple electrolyte such as sodium chloride, and the composite particles are subsequently used in formulating an aqueous coating composition, the film formed from the coating composition is likely to have adversely increased water sensitivity due to the presence of the additional salt. On the other hand, in some embodiments of the process of the present invention, it may be desirable to adjust the ionic strength of the aqueous medium by addition of a salt.

The surface potential of the inorganic material particles can be adjusted in a number of different ways. As discussed above, the particles can be pretreated to provide inorganic surface coatings, such as coatings of silica, aluminum oxide, or mixtures of silica and aluminum oxide, on titanium dioxide particles. In addition, small molecular species, such as silanes or titanates, can be adsorbed on and reacted with surface of the inorganic material particles, and the resulting surface sites can be subsequently modified chemically to provide surface charges. Examples of such species include N-2-aminoethyl-3-aminopropyltrimethoxy silane, 3-aminopropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, and vinyltriacetoxysilane. Alternatively, species having the desired charge, or which can be modified subsequently to have the desired charge, can be simply adsorbed to the surface of the inorganic material particles.

The selection of additives for adjusting the surface charge of the inorganic material particles depends on whether the surface charge on the particle needs to be raised or lowered. Additives which can be employed for the purpose of making the surface charge more negative include commonly available anionic surfactants and polysoaps, while a variety of monomeric and polymeric amino compounds or their quaternary derivative compounds can be employed if a less negative surface charge is desired.

Examples of suitable anionic surfactants include anionic polyelectrolyte pigment dispersants, such as polyacrylic acid, polymethacrylic acid, copolymeric acids including copolymeric acids including copolymerized maleic acid,

polyphosphates such as potassium tripolyphosphate, ammonium, alkali metal, alkaline earth metal, and lower alkyl quaternary ammonium salts of: sulfosuccinates such as di(C<sub>7</sub>-C<sub>25</sub>)alkylsulfosuccinates and higher alkyl sulfosuccinates, such as octyl sulfosuccinate; sulfates such as the higher fatty alcohol sulfates, for example, lauryl sulfate; sulfonates including aryl sulfonates, alkyl sulfonates, and the alkylaryl sulfonates, for example, isopropylbenzene sulfonate, isopropyl naphthalene sulfonate and N-methyl-N'-palmitoyltaurate, isothionates such as oleyl isothionate; and the like. Additional examples include the alkylaryl poly(ethyleneoxy) ethylene sulfates, sulfonates and phosphates, such as t-octyl-phenoxypoly(ethyleneoxy)ethylene sulfates and nonylphenoxy-poly(ethyleneoxy)ethylene phosphates, either having one to seven oxyethylene units.

Examples of suitable monomeric and polymeric amino compounds for reaction with excess negative surface charges on the inorganic material particle surface include alkylbenzylammonium halides such as diisobutylphenoxyethoxyethyl dimethylbenzyl ammonium chloride, tertiary amines formed by ethoxylation of primary amines such as primary tallow amines, imidazoline and piperazine derivatives, 2-methyl-2-aminomethylpropanol, and the like.

Two important properties of the polymeric latex for the purpose of the process of the invention are the glass transition temperature of the polymeric latex and the amount of acid functionality in the polymeric latex. While the chemical composition of a polymeric latex binder is important for achieving the resultant properties of the coating or film when the polymeric latex also acts as the binder, the glass transition temperature and amount of acid functionality in the polymeric latex are important in the adsorption process. The amount of acid functionality at the surface of the polymeric latex particles is believed to be especially important, as it is believed to relate directly to the surface charge density and zeta potential of the polymeric latex particles. In a presently preferred embodiment of the present process, a polymeric latex is employed by a process which preferentially provides acid functionality at the surface of the

polymer latex particles.

Another combination of two important properties of the polymeric latex for the purpose of the process of the invention are the glass transition temperature of the polymeric latex and the latex surface charge density. The latex surface charge density is closely related to the surface potential of the polymeric latex particles, and depends on such factors as the nature, amount and distribution or residual ionic initiator fragments in the latex, and the nature, amount, and distribution of carboxyl or other acid functionality in the polymeric latex. While the chemical composition of a polymeric latex binder is important for achieving the resultant properties of the coating or film when the polymeric latex also acts as the binder, the glass transition temperature and amount of acid functionality in the polymeric latex are important in the adsorption process. The amount of acid functionality at the surface of the polymeric latex particles is believed to be especially important, as it is believed to relate directly to the surface charge density and zeta potential of the polymeric latex particles. In a presently preferred embodiment of the present process, a polymeric latex is employed by a process which preferentially provides acid functionality at the surface of the polymer latex particles.

Examples of polymerization processes which preferentially provide surface acid are described in K. L. Hoy, J. Coat. Tech., 51, 27-41 (1979).

While the adsorption of the selected polymeric latex onto the inorganic material particles can occur rapidly, the adsorption may be reversible or irreversible with time. There are several factors which favor irreversible adsorption. For example, when copolymerizable dihydrogen phosphate-functional monomers are employed in preparing the polymeric latex particles, irreversible adsorption has been found to be favored, as well as when copolymerized itaconic acid is employed. Irreversible adsorption is also favored when the glass transition temperature of the polymeric latex is relatively low (such as less than about 50 C) or when the amount of acid functionality in the emulsion polymer is relatively high (such as greater than about 2 weight percent, or more typically, 0.02 moles of acid per 100 g of polymer solids).

In some applications, especially some coatings applications, when a selected

polymeric latex which irreversibly adsorbs onto the inorganic material particles is employed in the process of the invention there is a threshold pigment volume concentration ("TPVC") for the corresponding fully formulated composition above which the performance changes significantly. This threshold PVC is dependent upon the composition of the polymeric latex used in the adsorption process. When the threshold PVC is exceeded, grit formation may begin to be significant. In coatings, the gloss and hiding is reduced. The critical PVC appears to correlate with the saturation PVC in the grind, and the concentration of the irreversibly adsorbing polymeric latex should preferably be at or above the saturation level regardless of the PVC in these applications.

When the polymeric latex selected for use in adsorbing onto the inorganic material particle also functions as the polymeric binder for the fully formulated composition it is preferred that the polymeric latex not desorb from the inorganic particle. This can be accomplished by either utilizing a soft (low Tg) polymeric latex or by increasing the concentration of acid in the polymeric latex.

The presence of conventional polyelectrolyte dispersants has an effect on the adsorption process of the present invention. While low concentrations of conventional water-soluble polyelectrolyte dispersants, for example in the case of  $\text{TiO}_2$ , on the order of about 0.2 weight percent or lower, have little adverse effect on the adsorption of selected polymeric latexes onto inorganic material particle surfaces, the use of higher concentrations of these conventional water-soluble polyelectrolyte dispersants can have a significant adverse effect upon the adsorption of the selected polymeric latexes onto inorganic material particle surfaces. The use of more than about 0.2 weight percent of polyacrylic acid-type polyelectrolyte dispersants has been found to preclude a selected polymeric latex from adsorbing onto the inorganic material particle surface.

It is believed, without intending to be bound by any particular explanation of the observed phenomenon, that the suppression of polymeric latex adsorption is due to the increase in the surface charge of the inorganic material particle from the presence of the polyelectrolyte dispersant. Accordingly, the process of the present invention can be carried out with a minimum of polyelectrolyte

dispersant present in the aqueous medium. However, the presence of low concentrations of conventional polyelectrolyte dispersants is believed to actually be beneficial for eliminating the presence of grit in the fully formulated composition. Preferably, in the case of titanium dioxide from about 0.1 to 0.2 percent by weight of a polyelectrolyte dispersant such as Tamol (trademark of Rohm and Haas) 731 dispersant (sodium salt of polymeric carboxylic acid) is used as a predispersant when a relatively low glass transition polymeric latex, suitable for a film-forming binder, is employed in the process of this invention, so as to minimize grit formation. In general grit formation is believed to increase with decreasing polymeric latex glass transition temperature, decreasing polymeric latex surface charge, and decreasing polymeric latex particle size. In addition, poor mixing is believed to increase grit formation.

In one presently preferred embodiment of the present invention, an emulsion polymerization process known to provide acid functionality preferentially at the surface of the polymeric latex particles is employed to prepare the polymeric latex for adsorption on the inorganic material particles. In this case, the level of polyelectrolyte dispersant in the pigment dispersion and the formulated coating may be higher, such as up to one percent or more of the weight of the inorganic material, depending on the specific polyelectrolyte dispersant employed. In this case, a weakly absorbing polyelectrolyte dispersant, such as Tamol SG-1 dispersant (ammonium salt of copolymer of carboxylic acid monomer and hydrophilic comonomer) can be employed at a high level such as one percent, while a strongly absorbing polyelectrolyte dispersant such as a polyacrylic acid dispersant, which strongly adsorbs to the surface of the inorganic material particles, and which displaces weakly adsorbed polyelectrolyte dispersants from the surface of inorganic material particles, may require use at lower levels.

In another presently preferred embodiment of the present invention, an emulsion polymerization process is used to prepare a polymeric latex from monomer mixture including one or more ethylenically polymerizable derivatives of phosphoric acid, such as one or more dihydrogen phosphate esters of an alcohol in which the alcohol also contains a polymerizable vinyl or olefinic



group, such as partial esters of phosphoric acid and 2-hydroxyethyl methacrylate. Examples of such partial esters are given above and include the monoester of phosphoric acid with hydroxyethyl methacrylate, the diester of phosphoric acid with hydroxyethyl methacrylate, and mixtures thereof. The resulting phosphoric acid ester-functional polymeric latex particles adsorb to titanium dioxide particles more strongly than polymeric latex prepared from monomer mixture which does not include phosphoric acid ester-functional monomer.

The improved performance of coatings formulations prepared by the present process is achieved even in the presence of substantial amounts of large particle size extenders, such as large size calcium carbonate and alumino silicate, sometimes employed in such formulations. The improvement is not lost upon the incorporation of large size inorganic or organic particles, such as extender pigment particles.

In addition, the improved properties achievable by use of the process of this invention are realized when the formulation is prepared with conventional thickeners of the associative and non-associative types; this improvement is not dependent upon the selected thickener.

The process of the present invention can significantly increase the hiding of titanium dioxide containing emulsion paint formulations (as determined by measuring the scattering coefficient of the paint) of the same PVC compared with the scattering coefficient of a paint formulation prepared by the use of conventional polyelectrolyte dispersants. An alternate way of expressing this improvement is that the process of the invention permits the reduction of the PVC of a 20% PVC titanium dioxide paint formulation by 20 percent while achieving the same scattering coefficient or degree of hiding as can be obtained by the use of a conventional polyelectrolyte pigment dispersant. This translates into a reduction of titanium dioxide use level of 40 pounds per hundred gallons of paint, or, at the current titanium dioxide price of 95 cents per pound, a 38 cent per gallon decrease in titanium dioxide raw material costs. The hiding improvement is increased as the titanium dioxide volume concentration of the paint formulation increases. The improvement provided by the process of the present invention is illustrated in Figure 5, which is a graph in which the

scattering coefficients of films formed from an aqueous coating composition prepared using the inventive process are plotted as a function of PVC and compared with the those of films formed from coating compositions prepared using a conventional process.

Furthermore, the improved performance of paint formulations prepared by the present process is achieved even in the presence of substantial amounts of large particle size extenders, such as calcium carbonate and aluminosilicate, typically employed in such formulations. In this regard the improved hiding is obtained by the controlled adsorption of the primary pigment, the titanium dioxide. This improvement is not lost upon the incorporation of other types of inorganic or organic particles, such as extender pigment particles.

In addition, the improved hiding achievable by use of the process of this invention is realized when the coating formulation is prepared with conventional thickeners of the associative and non-associative types; this improvement is not dependent upon the selected thickener. This result is surprising and contrary to the result typically encountered when paints are formulated using conventional polyelectrolyte dispersants. In such conventional systems the hiding property of the formulated paint can vary greatly as a function of the thickener employed. The controlled adsorption process of the invention therefore offers paint formulators a greater choice in selecting thickeners for the final paint formulation without concern over the choice of thickener adversely affecting the final hiding properties of the paint.

Furthermore, in addition to improving the hiding of paint formulations, the process of this invention also has been found to advantageously improve the gloss, high shear viscosity, scrub resistance, and early blister resistance and metal marking resistance of paint formulations compared with paint formulations dispersed with conventional polyelectrolyte dispersants, as well as improving the corrosion resistance of paint formulations.

The process of the invention may be carried out in a number of alternative manners. For example, the polymeric latex particles can be selected so that they will serve as film-forming binder for the product formulated using the composite particles. Alternatively, the polymeric latex particles can be selected so

that they are not film-forming in the formulated product. In either case, the polymeric latex particles can be selected for use in dispersing the titanium dioxide particles, or for adsorption to titanium dioxide particles previously otherwise dispersed.

The process of the invention may be carried out in a number of alternative manners.

In one embodiment the surface charge of the inorganic material particles is adjusted and then the surface charge-adjusted inorganic material particle is simply milled directly with the polymeric latex. In another embodiment, the inorganic material particles, having their surface charge adjusted as necessary, are pre-dispersed in the absence of the polymeric latex. This is followed by blending with the polymeric latex under circumstances by which adsorption does not occur and then adjusting the medium until adsorption does occur, such as by altering the pH of the medium.

The process can involve the direct grinding of dry inorganic material particles in water with polymeric latex. In contrast with conventional pigment dispersion processes, the pigment dispersion process employed in the present invention is useful to prepare a concentrated pigment dispersion wherein the final concentration of pigment in the coating composition can be obtained directly in this one step without the formation of grit.

In carrying out the process of the present invention, it may be desirable to adjust the pH of the aqueous solution used for carrying out the process to a pH in the range of from about a pH of 6 to a pH of about 10.

Many different sizes of inorganic material particles can be employed in the process of the present invention, ranging from relatively small particle size, such as on the order of 100 nm, up through large particle size extender pigments, on the order of ten thousand nanometers, typically included in many types of formulations to reduce raw material costs. Examples of inorganic materials which can have large particle size and be used in the present process include calcium carbonate, alumino-silicate, amorphous silica, and the like. Mixtures of particles differing in chemical identity, particle size, or both, can be used.

For example, in addition to the titanium dioxide particles, which are typically

of relatively small particle size, on the order of 200-250 nm, other pigment particles, such as the large particle size extender pigment particle typically included in many types of coating formulation to reduce new material costs, can also be employed in addition to the titanium dioxide pigment particles in the process of the present invention. Examples of large particle size extender pigment particles which can be used include calcium carbonate, alumino-silicate, amorphous silica, and the like.

Similarly, the aqueous medium in which the inorganic material particles are ground with the polymeric latex dispersant can also include water-miscible solvents, such as glycols and glycol ethers, such as conventional in the coatings arts. Examples of water-miscible solvents employed include propylene glycol, ethylene glycol, ethylene glycol monomethyl ether, and the like.

Aqueous coating compositions are frequently formulated at alkaline pH to stabilize anionically charged latex binder against agglomeration and for other reasons. The principles of formulating aqueous coating compositions are reviewed, for example, in Formulation of Organic Coatings (N.I. Gaynes ed. D. Van Nostrand Co. Inc. Princeton, NJ 1967) at pp. 189-230.

The present invention provides aqueous dispersions of composite particles which can be used in a variety of applications. In some cases, in which a "soft" (i.e. low glass transition temperature) polymeric latex has been used to form the composite particles, the resulting aqueous dispersion can be used as is, or with the addition of other components, the soft adsorbed polymeric latex serving as binder for the composition. In other cases, additional polymeric latex will be added in formulating aqueous compositions for various applications, and the additional polymer latex will serve as the product binder in addition to or instead of the adsorbed polymeric latex.

Often the binder-forming latex polymer particles contain carboxyl functional groups. Under suitable conditions, the carboxyl groups are ionized and the resultant charges on the latex particle surface electrostatically stabilize the latex against premature agglomeration. Often a volatile base, typically ammonia, is used to adjust the pH of the coating composition. When the coating composition is applied to a substrate to be coated, the volatile base is lost and the pH of the

coating composition drops, destabilizing the latex particles of the binder and thus encouraging agglomeration to form a continuous binder film.

In addition to binder-forming polymeric latex particles and composite polymeric latex-inorganic material particles, aqueous coating compositions prepared according to the process of the present invention can include typical coatings ingredients. For example, they can include extender pigments as noted above such as calcium carbonate, amorphous silica, and the like; defoamers; biocidal agents such as zinc oxide, 2-N-octyl- 4-isothiazole-3-one, and phenyl mercuric acetate; coalescing agents such as diethylene glycol monoethyl ether acetate and ethylene glycol monobutyl ether acetate; plasticizers such as dialkyl phthalates including dibutyl phthalate, dioctyl phthalate and the like; freeze-thaw stabilizers such as ethylene glycol, propylene glycol and diethylene glycol; nonionic wetting agents such as polyethylenoxylates of fatty acids, alkanols, alkylphenols, and glycols; polyelectrolyte pigment dispersants at low levels; thickeners such as polyelectrolyte and cellulosic thickeners; rheology control agents such as associative thickeners and the like; colorants such as colored pigments and dyes; perfumes; cosolvents and the like.

The performance property improvements which can be realized by the process of the present invention are not limited to coatings and paint formulations. The present process is useful in other formulations utilizing other types of inorganic particles. For example in the case of conventional emulsion polymer-based pressure sensitive adhesive formulations it would be desirable from a cost perspective to utilize extenders without compromising on performance, however, the use of extenders in such formulations typically can not be accomplished with a significant reduction in properties such as, for example, peel resistance and tack. Because of the ability of the adsorption process of the invention to effectively disperse extender particles in a pressure sensitive film, we have found it possible to utilize certain inorganic particle extenders, such as, for example, silica, in pressure sensitive adhesive formulations with an increase in peel, shear and tack properties particularly at high filler loadings as compared with the same formulation using conventional dispersants for the extender pigment. The ability to obtain improved performance properties while

at the same time reducing the cost of an pressure sensitive adhesive formulation is another important result of the process of the present invention. This result is not limited to the use of silica as an extender for pressure sensitive adhesive formulations. We have also found that calcium carbonate can be used as a filler in roof mastic formulations by employing the adsorption process of the invention. In this regard we have found that roof mastics prepared by the process containing calcium carbonate filler exhibited lower modulus together with improved stress, elongation, and toughness especially at high filler loading. Conversely, by utilizing the adsorption process of the invention higher concentrations of inorganic particle filler can be used without attrition in the mechanical properties of the roof mastic.

Similarly, the process of the present invention has been found useful for preparing inorganic particle-filled binders for textiles and nonwovens, including binders for fiberfill. In this case, it may be desirable to entrain air in the binder by frothing before application to the substrate material.

The adsorption process of the invention is also useful in preparing coatings for paper. Clay is used as a filler in paper coatings but clay particles tend to align themselves together in such a way as to create undesirably high gloss in the coated paper. We have found that the adsorption process of the invention can be utilized to disperse clay particles and lower the gloss of coated paper and cardboard substrates. Furthermore, we have also found that the coated substrates are smoother and stronger than conventional paper coatings prepared by conventional techniques.

As in the case of adhesives, fillers are typically not employed at significant amounts in fiberfill binders. We have found that the adsorption process of the invention can be used to disperse clay and calcium carbonate in such applications. Furthermore the adsorption process of the invention permits the elimination of conventional polyelectrolyte dispersants and has been demonstrated as improving the washability, both wet and dry, as well as the wet and dry tensile strength of the fiberfill as compared to conventionally dispersed filler-containing fiberfill materials. Other coating systems such as for example roof mastic coating formulations employing inorganic particles as pigments,

fillers and extenders can be improved by the use of the process of this invention.

The illustrative examples which follow illustrate the process of the present invention as a function of the parameters of the selected emulsion polymer and the adsorption achieved. These examples will aid those skilled in the art in understanding the present invention; however, the present invention is in no way limited thereby. In the examples which follow, percentage composition is by weight, unless otherwise noted.

In the following Examples, reference shall be made to the following Figures:

Fig. 1a shows three schematic illustrations of agglomerate formation.

Fig. 1b shows energy diagrams for agglomerate formation.

Fig. 1c shows energy diagrams for agglomerate formation.

Fig. 1d is a schematic illustration of a preferred embodiment of the process of the present invention.

Fig. 2 is a schematic illustration of the distribution of inorganic particles, such as titanium dioxide particles, in a coating film formed from an aqueous composition prepared using a conventional prior art process.

Fig. 3 is a schematic illustration of the distribution of inorganic particles, such as titanium dioxide particles, in a coating film formed from an aqueous coating composition prepared using the process of the present invention.

Fig. 4 is a schematic representation of a an inorganic particle, such as a titanium dioxide particle, and a polymeric latex particle for illustration of the attractive and repulsive forces relating to heteroparticle adsorption.

Fig. 5 is a graph of the scattering coefficients of films formed from prior art coating compositions including a polyelectrolyte dispersant and films formed from coating compositions prepared using the process of the present invention, as functions of pigment volume concentration.

Fig. 6a is a scanning electron micrograph of composite particles prepared according to the process of the present invention.

Fig. 6b is a scanning electron micrograph of a mixture of titanium dioxide and polymeric latex particles prepared according to a prior art process.

Fig. 7 is a transmission electron micrograph showing composite particles prepared according to the process of the present invention.

Fig. 8a is a graph of the adsorption of polymeric latex on titanium dioxide particles for pigment grinds exemplifying the process of the invention as a function of grind PVC.

Fig. 8b is a graph of the logarithm of grind viscosity of the pigment grinds of Fig. 6a as a function of grind PVC.

Fig. 8c is a graph of the zeta potential of the composite particles formed in the pigment grinds of Fig. 6a as a function of grind PVC.

Fig. 9 is a graph of Kubelka-Munk scattering coefficient as a function of % PVC for a series of paints prepared according to the process of the present invention and compared with those for a series of conventionally dispersed paints.

Fig. 10a is a graph of Kubelka-Munk scattering coefficient as a function of grind PVC for a series of paints preparing according to the process of the present invention and storing a critical PVC.

Fig. 10b is a graph of 60° gloss as a function of grind PVC for the paints of Fig. 8a.

Fig. 10c is a graph of grit as a function of grind PVC for the paints of Fig. 8a.

Fig. 11 is a schematic illustration of another preferred embodiment of the process of the present invention.

Fig. 12 shows electron microscope images of composite particles.

One embodiment of the process of the present invention is illustrated schematically in Figure 1d. A powder of inorganic material pigment 10, such as  $\text{TiO}_2$  particles, including inorganic material particles 12, partially aggregated or agglomerated (by van der Waals, or contact forces, or by moisture, or the like), is mixed with an aqueous dispersion 20 of polymeric latex particles 22, each polymeric latex particle 22 having a greater negative surface potential than the inorganic material particles 12. If desired, a small amount of an aqueous medium (not shown) can be added to reduce the concentration of the particles, while typically the aqueous dispersion 20 of polymeric latex particles 22 will supply a satisfactory amount of aqueous medium for the dispersion of the inorganic material pigment 10. The mixture of inorganic material pigment 10



and the aqueous dispersion 20 is subjected to shear forces in a disperser (not shown), and the polymeric latex particles 22 spontaneously adsorb to the surface of inorganic material particles 12 to form a slurry or pigment grind 30 of composite particles 32 dispersed in the aqueous medium. Depending on conditions, the spontaneous adsorption can occur over the course of a few seconds, or may require up to several days. Without the addition of the polymeric latex particle and the application of shear forces by mixing, the inorganic material particles may form homo-aggregates, as conditions are preferable selected so that the inorganic material particles are slightly unstable with respect to homo-coagulation.

Figure 1d further illustrates the addition of a second aqueous dispersion 40 of another variety of polymeric latex particles 42 to the slurry 30 of composite particles 32 to form a formulated coating composition 50 including a mixture of composite particles 32 and second polymeric latex particles 42. In addition, other components such as low molecular weight cosolvents, plasticizers, thickeners, anti-fungal and antibacterial agents, stabilizers and the like can be added (not shown) to provide a fully formulated composition, such as a coating composition or paint, or an adhesive, etc. The fully formulated composition is then applied by conventional means to a surface 62 and permitted to dry and cure, thus forming a film 60 in which the inorganic material pigment particles 12 are imbedded in a continuous polymeric film 64 formed from the first variety of polymeric latex particles 22 and the second variety of polymeric latex particles 42. The spacing of the inorganic material particles 12 in the film 60 is not random, but instead is improved in comparison with prior art coatings films, allowing better distribution spacing and/or ability to more closely pack and increase the concentration, such as to provide better opacity.

One embodiment of the process of the present invention is illustrated schematically in Figure 11. A powder of titanium dioxide pigment 110 including titanium dioxide particles 112, partially aggregated or agglomerated (by van der Waals, or contact forces, or by moisture, or the like), is mixed with an aqueous dispersion 120 of a polyelectrolyte dispersant 122, each polyelectrolyte dispersant macromolecule 122 having a greater negative surface potential than the titanium

dioxide particles 112. Typically, an amount of an aqueous medium (not shown) is added to reduce the concentration of the particles. The mixture of titanium dioxide pigment 110 and the aqueous dispersion 120 is subjected to shear forces in a disperser (not shown), and the polyelectrolyte dispersant macromolecules 122 spontaneously adsorb to the surface of titanium dioxide particles 112 to form a slurry or pigment grind 130 of dispersed titanium dioxide particles 132 in the aqueous medium. Without the addition of the polyelectrolyte dispersant and the application of shear forces by mixing, the titanium dioxide particles may form homo-aggregates, as conditions are preferable selected so that the titanium dioxide particles are slightly unstable with respect to homo-coagulation.

Figure 11 further illustrates the addition of a second aqueous dispersion 140 including a mixture of two varieties of polymeric latex particles 142 to the slurry 130 of dispersed titanium dioxide particles 132 to form initially a formulated coating composition 150 including a mixture of dispersed titanium dioxide particles 132 and the two varieties of polymeric latex particles 142. The mixture of polymeric latex particles 142 includes a first type of polymeric latex particle 144 selected to adsorb strongly to the dispersed titanium dioxide particles 132 to form composite particles 46 including both a titanium dioxide particle 146a and a plurality of adsorbed selected polymer latex particles 146b. The selected polymeric latex particles 146b have an effective glass transition temperature which is between about room temperature or about 20°C and about 90°C, and more preferably between about 50°C and 90°C. In addition, the mixture of polymeric latex particles 142 includes a second type of polymeric latex particle 148 having a relatively low effective glass transition temperature, such as below about 10°C, and serving ultimately to form a binder for the the composite particles 146. In addition, other components such as low molecular weight cosolvents, plasticizers, anti-fungal and anti-bacterial agents, stabilizers and the like can be added (not shown) to provide a fully formulated coating composition. The fully formulated coating composition is then applied by conventional means to a surface 162 and permitted to dry and cure, thus forming a coating film 160 in which the composite particles 146 including the titanium dioxide pigment particles 112 are imbedded in a continuous polymeric film 164 formed from the

second variety of polymeric latex particles 142. The spacing of the titanium dioxide particles 112 in the film 160 is not random, but instead is improved in comparison with prior art coatings films, so as to provide enhanced opacity.

Figure 2 schematically illustrates the distribution of inorganic material particles in a coating film formed from an aqueous composition prepared using a conventional prior art process. After thorough mixing, the particles tend to be distributed in a random manner through the film. In the case of  $\text{TiO}_2$  particles, such random distribution leads to inefficient light scattering. In contrast, Figure 3 schematically represents the distribution of inorganic material particles in a coating film formed from an aqueous coating composition using the process of the present invention. In this case, the particles are more regularly distributed in the film. In the case of  $\text{TiO}_2$  particles, there is a better light scattering. In addition, fewer particles will provide a desired degree of opacification and the coating PVC can be lower than conventional dispersion methods.

It is believed that the controlled adsorption effected by the process of the present invention, at least in the case in which repulsive forces are provided by surface charge, can be understood by reference to the heteroparticle interaction theory of Hogg, Healy and Fuerstenau, which provides that the potential energy  $V_R$  resulting from the repulsion of like charges on particles of two different radii,  $a_1$  and  $a_2$ , and having differing surface potentials,  $P_1$  and  $P_2$ , in a aqueous medium with dielectric constant  $c$ , is given by Equation I:

$$V_R = [ca_1a_2(P_1^2 + P_2^2)/4(a_1 + a_2)] [2P_1P_2/(P_1^2 + P_2^2) * \ln[(1 + e^{-Kd})] + \ln(1 - e^{-2Kd})]$$

(I)

In Equation I  $K$  is a constant, the reciprocal of the so-called Debye length, inversely proportional to the square root of the ionic strength of the medium and  $d$  is the distance between the centers of the particles. In addition, for small particle separations, the van der Waals attractive potential  $V_A$  is approximated by Equation II:

$$V_A = -Aa_1a_2/6(a_1 + a_2)d \quad \text{(II)}$$

In Equation II,  $A$  is the Hamaker constant for the heteroparticle system. A qualitative plot of the net potential energy,  $V_T = V_R + V_A$ , as a function of the

particle separation distance  $d$  for a pair of particles with differing surface charges is given in Figure 4. The plot shows an energy barrier to coagulation at  $d_{\max}$ . If the energy barrier is less than about 10 kT, a mixture of the hetero particles is relatively unstable to coagulation, so that formation of composite particles can occur. However, too low an energy barrier to heterocoagulation, such as on the order of about 2 or 3 kT, will lead to too rapid a heterocoagulation process, and to the formation of agglomerates including more than a single inorganic material particle, rather than the desired composite particle including no more than a monolayer of adsorbed polymeric latex particles. Similarly, the height of the energy barrier is believed to be related to the rapidity with which composite particles are formed. The height of the energy barrier is seen to be determined by a number of parameters which may be adjustable to provide a mixture stable with respect to gross heterocoagulation, but which provides composite particle formation at a desired rate. For example, the height of the barrier increases with increasing particle size and surface potential, but decreases with increasing ionic strength and increasing Hamaker constants. By adjusting these parameters it is often possible to avoid gross heterocoagulation, while obtaining composite particle formation on a time scale that can be varied from on the order of the time of mixing to on the order of several days or more. The plot also shows a local minimum at  $d_{\min}$ , corresponding to an adsorbed particle pair.

In the examples, the following abbreviations are used:

AA acrylic acid

AMPS 2-acrylamido-2-methyl-1-propanesulfonic acid

IA itaconic acid

MAA methacrylic acid

EA ethyl acrylate

BA butyl acrylate

MMA methyl methacrylate

PSA pressure sensitive adhesive

DI deionized

### Example 1

A polymeric latex (46.2% solids) having a monomer composition of 46 BA/ 50.5 MMA/ 3.5 MAA was prepared using a conventional gradual-addition, batch polymerization process. The glass transition temperature ( $T_g$ ) calculated from the monomer composition by the method of Fox was 10°C. The polymeric latex was found to have an average particle size of 117 nm using a Brookhaven BI-90 light-scattering instrument to measure the particle size. The weight percent of methacrylic acid monomer on polymer solids was calculated to be 3.5 percent. 193 g of the polymeric latex was placed in a stainless steel grind bucket and the pH of the latex was adjusted to 11 by addition of ammonia. The bucket was positioned in a high speed disc disperser and mixing was begun at low speed while cooling in ice. 216 g of Ti-Pure (trademark of Du Pont de Nemours Corp.) R-900 grade rutile titanium dioxide pigment was slowly added to the bucket. Mixing speed was increased and water added as necessary to maintain good grinding action. Defoamer (Colloid 643) was added as needed. After mixing was complete, grinding was continued at high speed for 15-30 minutes. This provided a pigment grind with a PVC of 40% and 45% volume solids. Immediately after grinding, a sample was removed and centrifuged. The characteristics of the latex and the titanium dioxide, and the grinding conditions, are summarized in Table IA.

The concentration of unadsorbed latex in the supernatant was determined gravimetrically and used to calculate the milligrams of latex adsorbed per gram of titanium dioxide. This procedure was repeated after one day and two days. The results are given in Table IA. This example illustrates that the adsorption process conditions can be adjusted so that adsorption is extremely rapid. The rapidity is illustrated by the fact that adsorption is virtually complete during the time of grinding (compare 406 mg/g absorbed immediately after grinding with 407 mg/g absorbed after 2 days).

### Examples 2 - 18

The process of Example 1 was repeated, except as follows: Acrylic polymeric latexes having the particle sizes and acid levels shown in Tables IA-ID were

substituted for the polymeric latex used in Example 1. The calculated Tg for the polymeric latexes is given in Tables IA-ID. The grinding conditions, specifically the pH, PVC, volume solids and the speed of the disc disperser were varied as shown in Tables IA-ID. In one case, Example 7, Ti-Pure R-902 titanium dioxide was substituted for the R-900 grade. Absorption was measured as in Example 1, and the results are given in Tables IA-ID.

The results in Tables IA-ID confirm the rapidity of the adsorption of the polymeric latex; in most cases the amount absorbed after a day or two days is the same, within experimental error, as that absorbed immediately. In addition, the data show that adsorption conditions can be adjusted so that the rate of adsorption can be reduced if desired. In particular, Example 5 shows that conditions can be selected so that complete adsorption does not occur upon mixing, but rather requires a more extended period, for example, on the order of as long as a day, or more.

Examples 12 through 16 illustrate the saturation level concept: As the PVC decreases (greater ratio of polymeric latex to titanium dioxide) the amount adsorbed increases only slightly indicating saturation of the titanium dioxide.

These results also demonstrate the high adsorption efficiency attainable by the process of the present invention for a wide range of latex compositions and grinding conditions. The high efficiency is illustrated by the fact that essentially complete adsorption of the latex is achieved when the amount of latex added is adjusted to provide close to the saturation level of the latex on the titanium dioxide. This is shown in particular by Examples 1, 10, 12, and 13 which demonstrate that 99% of the total latex added is adsorbed on the titanium dioxide.

These examples also show that the level of adsorption is sensitive to the latex particle size but relatively insensitive to variables such as titanium dioxide grade (Examples 6 and 7), latex monomer composition, latex acid level and type, grinding conditions, such as the dispersion disc speed (Examples 11-13), pigment volume concentration, and volume solids.

Table IA

<u>Example</u>	1	2	3	4	5
<u>Latex:</u>					
Particle					
Size (nm)	117	76	113	117	67
Acid type	MAA	MAA	AMPS	MAA	MAA
Acid level (%)	3.5	7	4.8	3.5	1
Tg (°C)	10	10	1	10	1
Titanium	—				
<u>dioxide:</u>					
	R-900	R-900	R-900	R-900	R-900
Grinding					
<u>conditions:</u>					
pH	11	9	9	9	11
RPM					
<u>%PVC</u>	40	40	40	40	40
% Volume					
<u>Solids</u>	45	32	38	40	40
mg latex added					
<u>per g TiO<sub>2</sub></u>	412	412	412	412	412
Adsorption					
<u>(mg/g):</u>					
Immediate	406	237	381	379	217
1 Day . . . . .	407	219	386	380	335
2 Days	407	219	388	380	312
% Adsorbed	99	53	94	92	76

Table IB

<u>Example</u>	6	7	8	9	10
<u>Latex:</u>					
Particle					
Size (nm)	112	113	53	111	164
Acid monomer	MMA	MMA	AA	AA	AA
Acid level (%)	1	1	1.3	1.3	1.3
Tg (°C)	105	105	9	9	9
<u>Titanium</u>					
<u>dioxide:</u>					
	R-900	R-902	R-900	R-900	R-900
<u>Grinding</u>					
<u>conditions:</u>					
pH	9	9	9	9	9
<u>RPM</u>					
<u>% PVC</u>	40	40	40	40	40
<u>% Volume</u>					
<u>Solids</u>	45	46	40	40	40
<u>mg latex added</u>					
<u>per g TiO<sub>2</sub></u>	412	412	412	412	412
<u>Adsorption</u>					
<u>(mg/g):</u>					
Immediate	376	336	204	371	410
1 Day	370	308	213	374	410
2 Days	371	306			
% Adsorbed	90	74	52	91	99



Table IC

<u>Example</u>	11	12	13	14	15
<u>Latex:</u>					
Particle					
Size (nm)	150	150	150	150	150
Acid type	MAA	MAA	MAA	MAA	MAA
Acid level (%)	1	1	1	1	1
Tg (°C)	10	10	10	10	10
<u>Titanium</u>					
<u>dioxide:</u>					
	R-900	R-900	R-900	R-900	R-900
<u>Grinding</u>					
<u>conditions:</u>					
pH	9	9	9	9	9
RPM	650	1500	3800	1500	1500
<u>% PVC</u>	40	40	40	30	20
<u>% Volume</u>					
<u>Solids</u>	40	40	40	40	40
mg latex added					
<u>per g TiO<sub>2</sub></u>	412	412	412	642	1100
<u>Adsorption</u>					
<u>(mg/g):</u>					
Immediate	383	410	409	475	459
1 Day . . . . .	395	410	410	438	455
2 Days					
% Adsorbed	96	99	99	68	41

	<u>Table ID</u>		
<u>Example</u>	16	17	18
<u>Latex:</u>			
Particle			
Size (nm)	150	150	150
Acid type	MAA	MAA	MAA
Acid level (%)	1	1	1
Tg (°C)	10	10	10
Titanium			
<u>dioxide:</u>			
	R-900	R-900	R-900
Grinding			
<u>conditions:</u>			
pH	9	9	9
RPM	500	1500	1500
<u>% PVC</u>	10	40	40
% Volume			
<u>Solids</u>	40	30	20
mg latex added			
<u>per g TiO<sub>2</sub></u>	2475	412	412
Adsorption			
<u>(mg/g):</u>			
Immediate	508	383	250
1 Day	503	399	337
2 Days			356
% Adsorbed	20	97	86

### Example 19

A 40% PVC latex-dispersed grind (Example 19) was prepared by mixing 111.82 g of water 152.48 g of latex, and 168.00 g of Ti-Pure R-900 titanium dioxide in a Waring blender on low speed for five minutes using a water-jacketed stainless steel blend container. The polymeric latex was similar to that of Example 6 except that the average particle size was 120 nm.

A conventionally dispersed control (Comparative Example 1) was prepared by mixing 111.82 g of water, 6.914 g of Tamol 731 dispersant, and 168.00 g of Ti-Pure R-900 titanium dioxide using a high speed disk disperser at about 4000 rpm for ten minutes. The speed was decreased to 1200 rpm and 152.48 g of polymeric latex was added while stirring for an additional ten minutes.

A portion of each grind was diluted to about one percent by volume with water, a small drop placed on a standard SEM sample holder, and the water allowed to evaporate. The dried samples were then sputter coated with gold and examined via scanning electron microscopy. The resulting micrographs (magnification of 20,000:1) are shown in Figure 6a (Example 19) and Figure 6b (Comparative Example 1).

Figure 6a shows "raspberry"-shaped composite particles resulting from the adsorption of the small latex particles on the surfaces of the larger titanium dioxide particles.

. . . . By contrast, the smooth titanium dioxide particles and the unadsorbed latex particles seen in Figure 6b demonstrate the absence of such adsorption under conventional grinding conditions.

. . . . These micrographs provide a direct visual confirmation of the adsorption process of the present invention.

Example 20

A 20% PVC latex-dispersed (Rhoplex AC-61) pigment grind was prepared as in Example 1 except that the following formulation was used:

<u>Component</u>	<u>Weight (g)</u>
Rhoplex AC-61 polymeric latex	246.88
propylene glycol	10
Colloid 643 defoamer	0.5
water	10
Ti-Pure R-900 titanium dioxide	102.36

A portion of this grind was diluted about 20:1 with water a a drop placed on a 200 mesh carbon grid. Excess liquid was blotted off to leave a thin film which was frozen instantaneously by immersing at liquid ethane held at a temperature of 77 K by a surrounding liquid nitrogen bath. The frozen sample was then examined by transmission electron microscopy while being maintained at a temperature of -165°C. A representative micrograph is shown as Figure 7. The micrograph shows composite particles in which the polymeric latex particles (the lighter objects) are adsorped on the surface of titanium dioxide particles (the darker objects).

Examples 21 - 27

The procedure of Example 1 was repeated except that 30% volume solids grinds of varying PVC were prepared (pH = 9) using a commercially available polymeric latex (Rhoplex AC-61 latex)(Rhoplex is a trademark of Rohm and Haas Company) having a particle size of 150 nm, and glass transition temperature of 9 C, and titanium dioxide (Ti-Pure R-900). Adsorption in milligrams of latex per gram of titanium dioxide was determined as in Example 1. Viscosity was measured using a Brookfield viscometer at 6 RPM and 60 RPM. Zeta potential

was measured in an aqueous medium comprising 15 mM KCL at a pH of 9 using a Malvern Zetasizer IIc instrument. The results of the measurements are given in Table II and shown in Figures 8a - 8c in which absorption, log (grind viscosity) and zeta potential are respectively plotted as functions of the grind PVC.

These results show that the composite latex-titanium dioxide particles prepared by the process of this invention have decreased grind viscosity and increased surface charge. The adsorption results shown in Figure 8a demonstrate that, at PVC's below about 40, sufficient latex is added to saturate the titanium dioxide surface with latex; that is, the latex charge is equal to or greater than the saturation level of the Rhoplex AC-61 polymeric latex on Ti-Pure R-900 titanium dioxide. At higher PVCs, however, there is insufficient latex present and the level of adsorption decreases with increasing PVC. As shown in Figure 8b grind viscosity is observed to be high at high PVCs where there is little latex adsorption, but low at low PVCs where adsorption is complete. This demonstrates that latex adsorption results in a profound lowering of grind viscosity. In a similar manner, as shown in Figure 8c, the surface charge density of the composite particle, as indicated by its zeta potential, is high at low PVCs where adsorption is maximized, but decreases as adsorption decreases at high PVCs. The higher surface charge of the latex-dispersed titanium dioxide is an indication of greater stability.

Table II

Example	Grind	Absorption	Zeta	<u>Grind Viscosity (cp)<sup>1</sup></u>	
	<u>PVC</u>	<u>(mg/g)</u>	<u>Potential</u>	<u>6 rpm</u>	<u>60 rpm</u>
Rhoplex					
AC-61	0	-	-95	-	-
21	10	388	-87	260	80
22	20	356	-87	62	39
23	30	354	-86	28	19
24	40	394	-83	100	111
25	50	273	-86	39,100	3,170
26	60	182	-83	118,000	10,300
27	80	68	-68	390,000	27,900
Ti-Pure	100	-	-50	-	-
R-900					

- 
1. Grind viscosity is measured using a Brookfield viscometer at the speed shown.

Examples 28 - 31

A 20% PVC latex-(Rhoplex AC-61) dispersed grind was prepared as in Example 1 (except as follows) according to the following formulation:

<u>Component</u>	<u>Weight (g)</u>
Rhoplex AC-61 latex	493.77
propylene glycol	20.00
Colloid 643 defoamer	8.00
Ti-Pure R-900 titanium dioxide	204.7

Analogous grinds were also prepared in which the Ti-Pure R-900 titanium dioxide was pre-dispersed with 0.05% to 1.0% by weight Tamol 731 polyacrylic acid dispersant (Tamol is a trademark of Rohm and Haas Company). Tamol 731 is a sodium salt of polymeric carboxylic acid. Pigment dispersion with one percent by weight polymeric carboxylic acid dispersant is considered conventional. In preparing these grinds, a conventional Tamol 731-dispersed grind was prepared first; latex (Rhoplex AC-61) was then added and the mixture milled on a high speed disk disperser for 15 minutes. Adsorption in milligrams of latex per gram of titanium dioxide was determined as in Example 1. The results of the absorption measurement are shown in Table III. These results show that the advantageous results of the process of this invention are realized even in the presence of low levels of conventional water-soluble polyelectrolyte dispersants. However, high levels of such dispersants (e.g. several tenths of a percent by weight or higher, typical of those levels used for conventional dispersion of titanium dioxide) can result in complete suppression of adsorption. This effect is believed to be attributable due to the increase in titanium dioxide surface charge which results from adsorption of the conventional polyelectrolyte dispersant and addition of other species which result in adjusting surface charge to an inappropriate level (here too high) should lead to similar behavior.

Table III

<u>Example</u>	<u>Dispersant</u>	<u>Adsorption</u> <u>(mg/g)</u>
28	AC-61	562
29	0.05% Tamol 731/AC-61	378
30	0.1% Tamol 731/AC-61	351
31	0.2% Tamol 731/AC-61	208
Comp. 2 <sup>1</sup>	0.3% Tamol 731/AC-61	-13
Comp. 3 <sup>1</sup>	0.5% Tamol 731/AC-61	-80
Comp. 4 <sup>1</sup>	1.0% Tamol 731/AC-61	-174

1. Comparative example.

Examples 32 - 44

The process of Examples 28-31 was repeated to provide 35% volume solids pigment grinds using titanium dioxide pre-dispersed with 0.05% Tamol 731 polyelectrolyte dispersant (Tamol is a trademark of Rohm and Haas Company). Tamol 731 is a sodium salt of polymeric carboxylic acid. Pigment dispersion with one percent by weight polymeric carboxylic acid dispersant is considered conventional. In preparing these grinds, a conventional Tamol 731-dispersed grind was prepared first; latex was then added and the mixture milled on a high speed disk disperser for 15 minutes. A series of polymeric latexes of varying particle size and glass transition temperature and containing varying amounts of acidic monomer were prepared, as given in Table IV. The polymeric latexes were prepared using a gradual-addition, batch process, with all of the acidic monomer being added in the monomer mixture, except in the case of Example 39, in which the acidic monomer was added in a manner known to provide a preferred distribution of acid functionality at the surface of the polymeric latex.

After equilibrating grind for one week, a sample was removed, diluted 1 part to 3 parts with water, and centrifuged. The concentration of unadsorbed latex in the supernatant was determined gravimetrically and used to calculate the



milligrams of latex adsorbed per gram of titanium dioxide.

To determine the reversibility of the latex adsorption, 1% polyacrylic acid (Tamol 963 dispersant) was added to a portion of the remaining grind and the mixture stirred for 15 minutes. After equilibrating for 1 week, latex adsorption was determined as before. This procedure was carried out immediately after the grind was made and after it had been allowed to equilibrate for 1 day and 1 week. The results are given in Table IV.

These results in Table IV show that the ability of polyacrylic acid to desorb previously adsorbed latex decreases with decreasing effective Tg and increasing surface acidity of the latex.

Although in Examples 32-44 the effective Tg is controlled either by modifying the latex monomer composition so as to modify the actual polymer Tg (Examples 32-35), or by the addition of a low molecular weight plasticizer (Example 36), other methods of adjusting the effective Tg should be similarly efficacious. Likewise, surface acidity is controlled in these Examples 32-44 by varying the level of acidic monomer (Examples 33 and 37-38), or by polymerization process to enhance the surface acid (Example 39), but other methods of influencing latex surface acidity should be equally satisfactory.

The combined effects of Tg and surface acidity are also clearly demonstrated by the results given in Table IV. While desorption decreases significantly on going from 2% to 5% methacrylic acid when the Tg equals 50°C (Examples 33 and 37), it actually increases slightly for the same change in acidity at Tg = 90°C (Examples 32 and 40).

The results in Table IV also demonstrate that the type of acid functionality greatly influences reversibility. Thus replacing methacrylic acid with phosphoethyl methacrylate results in a decrease in desorption (Examples 37 and 41). A similar decrease in reversibility is obtained by replacing methacrylic acid with itaconic acid (Examples 33 and 42).

Table IV also shows that reversibility is not significantly effected by latex particle size (Examples 33 and 43 and Examples 35 and 44).

Table IV

<u>Example</u>	<u>Part. Size (nm)</u>	<u>Tg (C)</u>	<u>Acidic Monomer</u>	<u>Total Latex (mg/g)</u>	<u>Adsorption (mg/g)</u>	<u>% Desorption<sup>1</sup> After Equilibration</u>		
						<u>Imd.</u>	<u>1d</u>	<u>1Wk</u>
32	69	92	2% MAA	158	142	99	97	80
33	65	49	2% MAA	158	122	101	8	51
34	63	29	2% MAA	158	127	110	33	2
35	86	10	1% MAA	280	276	29	31	13
36	63	29 <sup>2</sup>	2% MAA	158	153	86	9	-2
37	64	51	5% MAA	158	137	91	67	20
38	66	52	10% MAA	158	132	95	7	2
39	64	51	5% MAA	158	137	64	1	0
40	73	94	5% MAA	158	152	109	105	97
41	56	54	2% MAA+ 2% PEM <sup>3</sup>	158	156	23	7	3
42	69	50	2% IA <sup>4</sup> . . . .	158	157	22	-1	-1
43	161	49	2% MAA	521	491	70	32	45
44	148	10	1% MAA	521	512. . . . .	49	16	8

1. Desorption values less than 0 and greater than 100 reflect experimental error in the desorption measurement and imply no desorption and complete desorption respectively.

2. Contains 10% Texanol coalescent (trademark of Eastman Kodak Co.), 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate.

3. PEM = phosphoethyl methacrylate.

4. IA = itaconic acid.

#### Examples 45 - 47

A typical conventionally dispersed 20% PVC gloss paint (Comparative Example 5) was prepared according to the following formulation.

Pigment grind:

<u>Component</u>	<u>Weight (g)</u>
water	20
propylene glycol	20
Colloid 643 defoamer	1
Tamol 731 dispersant	8.22
Ti-Pure R-900 titanium dioxide	204.72

These components were milled on a high speed disk disperser to form a pigment grind, and were letdown at a slower speed with the following:

<u>Component</u>	<u>Weight (g)</u>
Rhoplex AC-61 polymer latex	493.77
Colloid 643 defoamer	4
Texanol coalescent	22.96
Triton GR-7M surfactant	2
propylene glycol	59
Nuosept 95 preservative	6
water and Natrosol 250 MR cellulosic thickener	175.03

The mix is thickened to a Stormer viscosity of of 90 KU by addition of an aqueous solution of the cellulosic thickener, and the pH of the mix is adjusted to 9 by addition of a concentrated ammonia solution. Rhoplex is a trademark of Rohm and Haas Co. Nuosept is a trademark of Nuodex, Inc. Natrosol is a trademark of Hercules, Inc.

Latex-dispersed analogs of Comparative Example 5 were prepared at 20% PVC (Example 45) and lower PVCs (Examples 46-47) by omitting the Tamol 731 dispersant and including the Rhoplex AC-61 polymeric latex in the grind. To prepare the latex-dispersed grinds, all wet ingredients were placed in an ice-cooled grind bucket and the Ti-Pure R-900 titanium dioxide was added while stirring slowly. Mixing speed was then increased to give a good vortex and milling was continued for 15 minutes. Kubelka-Munk scattering coefficients were determined for all paints using a modification of ASTM D 2805-70. The results of these measurements are given in Table V.

These examples demonstrate that there is a substantial increase in hiding as reflected by the Kubelka-Munk scattering coefficients when titanium dioxide is dispersed with polymeric latex according to the process of this invention rather than when the titanium dioxide is dispersed with a conventional water-soluble,

polyelectrolyte dispersant. For example, the scattering coefficient measured for the 20% PVC gloss paint in which the titanium dioxide was dispersed conventionally was 7.45 (Comparative Example 5) while the scattering coefficient for the 20% PVC gloss paint prepared according to the present invention was 8.65 (Example 45).

The increased scattering efficiency of latex-dispersed titanium dioxide allows paints to be formulated at significantly lower PVCs without loss of hiding power, greatly reducing the usage of expensive titanium dioxide. This is shown by the fact that the paint of Example 47, which has a PVC of only 16%, has about the same scattering coefficient as that of Comparative Example 45 which has a PVC of 20%, twenty-five percent higher.

Table V

.....			Scattering
Example	Dispersant	%_PVC	Coefficient
Comp. 5 <sup>1</sup>	Tamol 731	20	7.45
45	AC-61	20	8.65
46	AC-61	18	7.99
47	AC-61	16	7.42

-----  
1. Comparative Example.

Examples 48 - 51

A series of latex-dispersed paints (Examples 48-51) and a series of conventionally dispersed paints (Comparative Examples 6-9), each series having 40, 30, 20, and 10% PVC, were prepared according to the formulation of Examples 45-47 except that the Rhoplex AC-61 latex was replaced with Rhoplex AC-235 latex, a commercially available latex intended for paint application, and the Texanol coalescent was omitted. Kubelka-Munk scattering coefficients were determined as in Examples 45-47. The results obtained are given in Table VI and shown in Figure 9.

These results show that the improved hiding obtained by dispersing titanium dioxide with latex according to the process of this invention is realized over a wide range of titanium dioxide PVCs. The greatest increases in the scattering coefficient are observed at high PVCs (Examples 50-51) where the distances between the individual titanium dioxide particles are small.

Table VI

<u>Example</u>	<u>% PVC</u>	<u>Scattering Coefficient</u>
48	10	4.25
Comp. 6 <sup>1</sup>	10	4.04
49	20	7.18
Comp. 7 <sup>1</sup>	20	6.60
50	30	9.40
Comp. 8 <sup>1</sup>	30	8.39
51	40	9.68
Comp. 9 <sup>1</sup>	40	8.61

---

1. Comparative example.

Examples 52 - 55

A typical conventionally dispersed flat paint (Comparative Example 10) containing 15% PVC titanium dioxide (Ti-Pure R-900) and 37% alumino-silicate extender (Minex 4) was prepared according to the following formulation:

## Pigment grind:

<u>Component</u>	<u>Weight (g)</u>
water	200
ethylene glycol	18
Colloid 643 defoamer	2
Tamol 731 dispersant	12.9
Natrosol 250MHR thickener	2.5
Ti-Pure R-900 titanium dioxide	180
Minex 4 alumino-silicate	280
(Minex is a trademark of Falconbridge Ltd.)	

The mixture was milled on a high speed disk disperser and letdown at a slower speed with the following:

Rhoplex AC-61 polymer latex	337.6
Colloid 643 defoamer	4
Texanol coalescent	15.7
Nuosept 95 preservative	6
water and Natrosol 250 MR cellulosic thickener solution	103.2

The paint was thickened to a Stormer viscosity of 95 KU, and the pH was adjusted to 9.5 by addition of ammonia.

Four latex-dispersed analogs (Examples 52-55) of Comparative Example 10 were prepared by omitting the Tamol 731 dispersant and including the Rhoplex AC-61 latex in the grind. The latex-dispersed grinds for these four paints were all prepared in a manner similar to Examples 45-47 but with the following variations: (1) Ti-Pure R-900 added before Minex 4 (Example 52); (2) Minex 4 added before Ti-Pure R-900 (Example 53); (3) separate latex-dispersed Ti-Pure

R-900 grind and Minex 4 grind prepared (Example 54); and (4) separate grinds, the Ti-Pure R-900 latex-dispersed, the Minex 4 conventionally dispersed with Tamol 731 (Example 55).

Kubelka-Munk scattering coefficients were determined as above. The results are given in Table VII. These results demonstrate that the improved hiding obtained by dispersing titanium dioxide with latex according to the process of this invention is realized even in the presence of substantial levels of the large particle size extenders typically used in higher PVC paints. The Minex 4 alumino-silicate had an average particle size of about 7.5 microns (National Paint and Coatings Association Raw Materials Index). Further, these results demonstrate that, in order to achieve the increased hiding, it is only necessary that the titanium dioxide be latex-dispersed, latex dispersion of the extender pigment is not required.

Table\_VII

<u>Example</u>	<u>Dispersant</u>	<u>Comments</u>	<u>Scattering Coefficient</u>
Comp. 10 <sup>1</sup>	Tamol 731	Control	4.16
52	AC-61	R-900 added before Minex 4	4.71
53	AC-61	Minex 4 added before R-900	4.83
54	AC-61/AC-61	separate R-900/ Minex 4 grinds	4.79
55	AC-61/ Tamol 731	separate R-900/ Minex 4 grinds	4.68

#### 1. Comparative example.

#### Examples 56 - 59

The latex-dispersed grinds of Examples 28-31 and Comparative Examples 2-4 were letdown to paints according to the formulation of Examples 45-47 to provide the paints of Examples 56-59 and Comparative Examples 11-13.

Kubelka-Munk scattering coefficients were determined, and the results are given in Table VIII along with results for a control paint conventionally dispersed with Tamol 731 dispersant (Comparative Example 14).

These results demonstrate that low levels of conventional pre-dispersants can be beneficial in cases where dispersing titanium dioxide with latex according to the process of this invention results in grit in the fully formulated paint, as with Example 57. In such cases, low levels of conventional predispersant eliminate the grit without seriously compromising hiding. However, levels of pre-dispersant which are too high (Comparative Examples 11-13, 0.3% - 1.0% by weight, respectively) suppress latex adsorption and with it the increased hiding which results from such adsorption.

Table VIII

Example	<u>Dispersant</u>	<u>Grit</u>	<u>Scattering Coefficient</u>
56	AC-61	Moderate	8.40
57	0.05% Tamol 731/AC-61	None	7.92
58	0.1% Tamol 731/AC-61	None	8.10
59	0.2% Tamol 731/AC-61	None	8.07
Comp. 11 <sup>1</sup>	0.3% Tamol 731/AC-61	None	7.59
Comp. 12 <sup>1</sup>	0.5% Tamol 731/AC-61	None	7.41
Comp. 13 <sup>1</sup>	1.0% Tamol 731/AC-61	None	7.18
Comp. 14 <sup>1</sup>	1.0% Tamol 731	None	7.17

---

1. Comparative example.

Examples 60 - 64

Latex-dispersed (Examples 60-64) and conventionally dispersed (Comparative Examples 15-19) paints were prepared according to the formulation of Examples 45-47 using five different thickeners, as given in Table IX.



Table IX

<u>Thickener</u>	<u>Type</u>	<u>Efficiency</u>
Natrosol 250MR	non-associative	
Acrysol RM-825 <sup>1</sup>	nonionic associative	High
Acrysol RM-1020	nonionic associative	Low
Acrysol TT-935	anionic associative	High
Acrysol RM-5	anionic associative	Low

-----  
 1. Acrysol is a trademark of Rohm and Haas Co.

Kubelka-Munk scattering coefficients were determined as above. Results are given in Table X. In each case, the hiding of the latex-dispersed paint was greater than the hiding of the conventionally dispersed paint. These results demonstrate that the improved hiding obtained by dispersing titanium dioxide with latex according to the process of this invention is realized with both non-associative and associative-type thickeners. Unlike paints based on conventional water-soluble dispersants, where the hiding can vary greatly from thickener to thickener, latex-dispersed paints show the same excellent hiding regardless of the type of thickener used.

Table X

<u>Example</u>	<u>Thickener</u>	<u>Scattering Coefficient</u>
60	Natrosol 250MR	8.44
Comp. 15 <sup>1</sup>	Natrosol 250MR	7.44
61	Acrysol RM-825	8.30
Comp. 16 <sup>1</sup>	Acrysol RM-825	7.76
62	Acrysol RM-1020	8.31
Comp. 17 <sup>1</sup>	Acrysol RM-1020	7.68
63	Acrysol TT-935	8.04
Comp. 18 <sup>1</sup>	Acrysol TT-935	7.17
64	Acrysol RM-5	8.07
Comp. 19 <sup>1</sup>	Acrysol RM-5	7.86

[1. Comparative example.]

Examples 65 - 79

Latex-dispersed gloss paints were prepared by the process of Examples 56-59 in which the Ti-Pure R-900 was pre-dispersed with 0.1% Tamol 731 dispersant. Pigment grinds were prepared as in Examples 28-31 but the amount of latex dispersant (Rhoplex AC-61) added to the grind was varied so as to give grind % PVCs of 20, 30, 40, 50, and 60. Binder latex (Rhoplex AC-61) was added to the letdown as needed to give a final paint % PVC of 20. Paints were thickened with Natrosol 250MR, Acrysol RM-1020, and Acrysol TT-935 thickeners. Kubelka-Munk scattering coefficients were determined as above, and 60 gloss was measured using a Pacific Scientific Glossgard II glossmeter. Grit was rated on a qualitative scale. Results are given in Table XI and plotted in Figures 10a-10c.

As noted above (Examples 32-44, Table IV), it appears that low  $T_g$  latexes (the  $T_g$  of Rhoplex AC-61 polymeric latex is 9 °C) adsorb irreversibly on titanium dioxide. The results shown in Figures 10a-10c and reported in Table XI demonstrate that, when an irreversible adsorbed latex is used to disperse titanium dioxide according to the process of this invention, there is a "critical" grind PVC above which paint performance deteriorates markedly. With Rhoplex AC-61 latex as the dispersing latex, this appears at about 40-50 % PVC. At PVCs above this level, hiding and gloss drop precipitously (60 % PVC, Examples 69, 74 and 79) and grit becomes severe. The saturation level for Rhoplex AC-61 polymer latex adsorbed on Ti-Pure R-900 titanium dioxide is measured to be about 400 mg/g (Examples 21-24, Table II), which is equivalent to a grind PVC of 41%. Thus, for an irreversibly adsorbed "soft" (that is, having a low effective glass transition temperature) latex, in order to obtain optimum performance sufficient latex must be charged to the grind to fully saturate the titanium dioxide surface.

Table XI

<u>Example</u>	<u>% Grind PVC</u>	<u>Thickener</u>	<u>Scattering Coefficient</u>	<u>Gloss</u>	<u>Grit</u>
65	20	Natrosol 250MR	8.37	60	none
66	30	"	8.21	59	none
67	40	"	7.97	60	moderate
68	50	"	7.85	58	moderate
69	60	"	5.12	19	severe
70	20	Acrysol RM-1020	8.12	65	none
71	30	"	7.80	65	none
72	40	"	7.93	65	none
73	50	"	7.88	65	moderate
74	60	"	5.34	18	severe
75	20	Acrysol TT-935	7.72	65	slight
76	30	"	7.85	65	slight
77	40	"	7.59	66	slight
78	50	"	7.31	63	moderate/ severe
79	60	"	5.25	21	severe

Examples 80 - 97

Latex-dispersed gloss paints were prepared by the process of Examples 65-79 in which the Ti-Pure R-900 was pre-dispersed with 0.05% Tamol 731 dispersant. Pigment grinds were prepared as in Examples 28-31 but a small, "hard" (i.e. high Tg) latex dispersant (66 nm, Tg = 92°C, 2% methacrylic acid) was employed, and the amount of latex dispersant added to the grind was varied so as to give grind % PVCs of 60, 65, 70, 75, 80, and 85. Binder latex (Rhoplex AC-61) was added to the letdown as needed to give a final paint % PVC of 20. Paints were thickened with Natrosol 250MR, Acrysol RM-1020, and Acrysol TT-935 thickeners as in Examples 65-79. Kubelka-Munk scattering coefficients, 60° gloss, and grit were determined as above. Results are given in Table XII.

As shown by Examples 32-44 above, absent special functional groups providing strong adsorption, high T<sub>g</sub> latexes adsorb reversibly on titanium dioxide particles. The results reported in Table XII for Examples 80-97

demonstrate that, unlike the situation demonstrated by Examples 65-79 for an irreversibly adsorbed latex, when a reversibly adsorbed latex is used to disperse titanium dioxide according to the process of this invention, paint performance is independent of grind PVC. Reversibly adsorbed polymeric latex dispersants can be displaced by the binder latex in fully formulated paints. Since binder latexes are generally "soft" (i.e. low glass transition temperature) and adsorb irreversibly, the titanium dioxide particles which were originally coated with reversibly adsorbed "dispersant latex" are believed to eventually become coated with irreversibly adsorbed "binder latex". Thus, extrapolating from the the results of Examples 80-97, it appears that optimum paint performance thus requires only that sufficient binder latex be present to fully saturate the titanium dioxide surface.

Table XII

<u>Example</u>	<u>% Grind PVC</u>	<u>Thickener</u>	<u>Scattering Coefficient</u>	<u>Gloss</u>	<u>Grit</u>
80	60	Natrosol 250MR	8.67	54	slight/ moderate
81	65	"	8.76	57	slight
82	70	"	8.58	57	moderate
83	75	"	8.32	58	moderate
84	80	"	7.84	59	slight/ moderate
85	85		7.97	58	moderate
86	60	Acrysol RM-1020	8.36	67	slight/ moderate
87	65	"	8.29	33	none
88	70	"	8.24	26	moderate
89	75	"	8.35	59	moderate
90	80	"	8.37	66	slight/ moderate
91	85		8.01	65	moderate
92	60	Acrysol TT-935	7.85	41	slight
93	65	"	8.15	54	none
94	70	"	8.34	60	slight/ moderate
95	75	"	8.18	60	slight
96	80	"	8.29	61	slight
97	85		7.88	59	slight

Examples 98 - 100

A conventionally dispersed 20% PVC gloss paint (Comparative Example 20) was prepared according to the following formulation.

## Pigment grind:

<u>Component</u>	<u>Weight (g)</u>
water	30
propylene glycol	20
Colloid 643 defoamer	1
Tamol 731 dispersant	8.19
Ti-Pure R-900 titanium dioxide	204.72

These components were milled on a high speed disk disperser to form a pigment grind and were letdown at a slower speed with the following:

<u>Component</u>	<u>Weight (g)</u>
Rhoplex AC-61 polymeric latex	493.76
Colloid 643 defoamer	4
Texanol coalescent	22.96
Triton GR-7M surfactant	2
propylene glycol	59
Nuosept 95 preservative	6
water and Natrosol 250MR cellulosic thickener	181.08

The mix is thickened to a Stormer viscosity of 80 Krebs Units ("KU") by addition of an aqueous solution of the cellulosic thickener, and the pH of the mix is adjusted to 9 by addition of ammonia.

A second conventionally dispersed 20% PVC gloss paint (Comparative Example 21) was also prepared according to the formulation of Comparative Example 20 except that the polymeric latex (Rhoplex AC-61), which has a particle

size of about 150 nm, was replaced with a polymeric latex of identical monomer composition but with a particle size of 86 nm ("Latex A", 38.7% solids).

A polymeric latex-dispersed analog (Example 98) of Comparative Example 20 was prepared using the following pigment grind formulation:

Component	Weight_(g)
water	30.62
propylene glycol	60
Colloid 643 defoamer	1
Tamol 731 dispersant	0.41
Ti-Pure R-900 titanium dioxide	204.72
Rhoplex AC-61 polymeric latex	493.76

To prepare the latex-dispersed grind, all components except the polymeric latex were milled on a high speed disk disperser to form an initial pigment grind. The polymeric latex was then added and milling was continued for 15 minutes while cooling with ice to give the final latex-dispersed grind. This was letdown at a slower speed to yield a paint (Example 98) with the same composition as Comparative Example 20 except for a slightly lower level of Tamol 731 dispersant.

A latex-dispersed analog (Example 99) of Comparative Example 21 was prepared in the same manner except that the Rhoplex AC-61 polymeric latex was replaced with Latex A.

A latex-dispersed 20% PVC gloss paint (Example 100) was prepared according to the following formulation using polymeric latex having a glass transition temperature of 49°C, a particle size of 65 nm, and having 2% methacrylic acid (Latex B, 37.9 % solids:

Pigment grind:

_____Component_____	Weight_(g)
water	36.62
propylene glycol	54
Colloid 643 defoamer	1
Tamol 731 dispersant	0.41
Ti-Pure R-900 titanium dioxide	204.72
Latex B	85.57
Texanol coalescent	3.24

To prepare the latex-dispersed grind, all components, except the Latex B and the Texanol coalescent, were milled on a high speed disk disperser to form an initial pigment grind. Then the Latex B and the coalescent were combined and added, and milling continued for 15 minutes while cooling with ice to give the final latex-dispersed grind. This was conditioned (to reduce desorption of the adsorbed Latex B) by being allowed to equilibrate for two days, and letdown at a slower speed with the following:

_____Component_____	Weight_(g)
Latex B	509.52
Colloid 643 defoamer	4
Texanol coalescent	19.72
Triton GR-7M surfactant	2
propylene glycol	25
Nuosept 95 preservative	6
water and Natrosol 250MR cellulosic thickener	81.8

The mix is thickened to a Stormer viscosity of 80 KU by addition of an aqueous solution of the cellulosic thickener, and the pH of the mix adjusted to 9 by addition of ammonia.

Kubelka-Munk scattering coefficients were determined for all paints as above.

The results are given in Table XIII.

These results confirm the substantial increase in scattering coefficient, which is a measure of the hiding power of the paint, obtained when titanium dioxide is dispersed with polymeric latex according to the process of the present invention. These results also show that the extent of this hiding increase decreases with decreasing particle size of the adsorbed polymeric latex. This is illustrated by the fact that the 150 nm polymeric latex of Example 98 shows an increase of 0.92 units in scattering coefficient relative to Comparative Example 20, while the 86 nm polymeric latex of Example 99 shows an increase of only 0.27 units over Comparative Example 21. These results also demonstrate that hiding increases with increasing glass transition temperature of the adsorbed polymeric latex. Thus, dispersing the titanium dioxide with the 65 nm,  $T_g = 49^\circ\text{C}$ , latex (Example 100) provides a scattering coefficient of 8.50, which is substantially higher than the coefficient of 7.67 obtained for the 86 nm,  $T_g = 10^\circ\text{C}$ , polymeric latex (Example 99), and even slightly higher than the scattering coefficient of 8.23 obtained for the much larger 150 nm,  $T_g = 10^\circ\text{C}$ , polymeric latex (Example 98).

Table XIII

<u>Example</u>	<u>Binder</u>	<u>Dispersant</u>	<u>Scattering Coefficient</u>	<u>Comment</u>
C. 201	AC-61	1% Tamol 731	7.31	control
C. 211	Latex A	1% Tamol 731	7.40	control
98	AC-61	0.05% Tamol 731 + AC-61	8.23	150 nm, $T_g=10^\circ\text{C}$ latex-dispersed
99	Latex A	0.05% Tamol 731 + Latex A	7.67	86 nm, $T_g=10^\circ\text{C}$ ..... latex-dispersed
100	Latex B	0.05% Tamol 731 + Latex B	8.50	65 nm, $T_g=49^\circ\text{C}$ ..... latex dispersed

---

1. Comparative example.



## Example\_101

A typical conventionally dispersed exterior flat paint (Comparative Example 22) was prepared according to the following formulation:

## Pigment grind:

<u>Component</u>	<u>Weight (g)</u>
water	58
methyl carbitol	59
Colloid 643 defoamer	1
Tamol 681 dispersant	8
Triton N-57 dispersant	4
Ti-Pure R-902 titanium dioxide	225
Minex 4 alumino-silicate	160
Icecap107 K clay	50
(Icecap is a trademark of Burgess Pigment Co.)	

The pigment grind was milled on a high speed disk disperser and letdown at a slower with the following:

<u>Component</u>	<u>Weight (g)</u>
Rhoplex AC-829 polymeric latex	370.3
Colloid 643 defoamer	3
Texanol coalescent	9.3
Polyphase AF-1 fungicide, (Troy Chemical Corp.)	4
Acrysol TT-935 thickener	13.4
water and Natrosol 250MR	190.4

The pH is adjusted to 9 with ammonia.

A latex-dispersed analog of the above was prepared by omitting the Tamol 681

dispersant and including a polymeric latex dispersant (Rhoplex AC-829) in the grind. To prepare the latex dispersed grind, all wet ingredients were placed in the grind bucket and the Ti-Pure R-902 added while stirring slowly. Mixing speed was then increased to give a good vortex. Early blister resistance was measured over a chalky substrate after drying overnight. Samples were rated according to ASTM blister standards (Pictorial Standards of Coating Defects published by the Federation of Societies of Coating Technology) after one hour in a fog box. Results are given in Table XIV, and show that the process of the present invention provides improved early blister resistance in comparison with a paint made using pigment dispersed with a conventional water-soluble dispersant.

Table XIV

<u>Example</u>	<u>Blister Rating</u>		<u>Size</u>	<u>Density</u>
	<u>Paint</u>			
Comp. 22	control		8	Medium Dense
101	latex-dispersed		none	-

## Examples\_102\_-\_105

A one percent Tamol 731-dispersed grind (Comparative Example 23) was prepared by mixing 9 g of water, 40 g of propylene glycol, 2 g of Colloid 643 defoamer, 8 g of Tamol 731 dispersant, and 200 g of Ti-Pure R-900 titanium dioxide using a high speed disk disperser, and the pH was adjusted to about 9 by addition of ammonia.

Additional grinds were prepared in a similar manner except that the 1 % Tamol 731 dispersant was replaced with 0.05 % Tamol 731 dispersant (Example 102) or with 0.05 % Tamol 731 dispersant and either 0.2% citric acid (Example 103), 0.21 % L-tartaric acid (Example 104), or 0.375 % sodium succinate (Example 105). The amount of water added was adjusted to give the weight percent titanium dioxide values listed in Table XV. The grind viscosities as measured using a Brookfield LVT viscometer at either 12 or 60 rpm are also given in Table XV.

Mixtures of these grinds with Rhoplex AC-61 polymeric latex were prepared by

adding the grind to the polymeric latex (1.132 g of polymeric latex per g of titanium dioxide) while stirring. Adsorption was then measured after two hours and after one, seven, and twenty-three days by diluting 8 g of the grind/polymeric latex mixture with 27 g of water, centrifuging, and determining the concentration of the unadsorbed polymeric latex in the supernatant gravimetrically. The results are given in Table XV as milligrams of polymeric latex adsorbed per gram of titanium dioxide.

20% PVC paints were prepared from each of the pigment grind/polymeric latex mixtures by letting down with 4 g of Colloid 643 defoamer, 22.64 g of Texanol coalescent, 2 g of Triton GR-7M surfactant, 59 g of propylene glycol, 6 g of Nuosept 95 preservative, 100.4 g of a 5% aqueous Natrosol 250 MR cellulosic thickener solution, and sufficient water to give a final volume solids of 30 %. pH was adjusted to about 9 by addition of ammonia.

Kubelka-Munk scattering coefficients were determined for all paints. 60° gloss was measured using a Pacific Scientific Glossguard II glossmeter. Grit was rated on a qualitative scale. The results of these measurements are also given in Table XV.

The results in Table XV demonstrate that low levels of small molecule co-dispersants can have a beneficial effect in the process of the present invention. Thus, tartaric acid (Example 104) and citric acid (Example 103) co-dispersants substantially reduce the grind viscosity compared to that observed in their absence (Example 102) without seriously reducing polymeric latex adsorption. Tartaric acid and citric acid also appear to have a favorable effect on grit formation. The citric acid-containing paint (Example 103) shows even less grit than does the conventionally dispersed 1% Tamol 731-dispersed control (Comparative Example 23). Gloss is also significantly enhanced by the presence of the citric acid co-dispersant.

Table\_XV

<u>Example</u>	<u>Comp23</u>	<u>102</u>	<u>103</u>	<u>104</u>	<u>105</u>
% Tamol 731	1.0	0.05	0.05	0.05	0.05
Co-dispersant	none	none	citric acid	tartaric acid	sodium succinate
Weight percent					
TiO <sub>2</sub> in grind	77.2	59.6	76.0	69.3	60.9
Grind viscosity (centipoise)	2,340	22,750	4,080	7,990	20,400
Adsorption (mg/g)					
2 hours	130	430	160	370	440
1 day	180	450	260	460	420
7 days	110	470	330	460	420
23 days	100	470	370	450	460
Scattering					
Coefficient	6.8	7.9	7.7	7.9	7.4
Gloss	52	57	62	58	41
Grit	slight	slight- moderate	none	slight	slight- moderate

## 1. Comparative example.

## Examples\_106\_-\_107

A multi-stage gradual addition process was employed to prepare an acrylate copolymer emulsion from monomer including 1.9 percent by weight methacrylic acid. The polymeric latex, Latex C, contained 44.7% solids with an average particle diameter of 166 nm. Latex C is believed to have a substantial proportion of acid functionality at the surface of the latex particle as determined by potentiometric titration. A modification of the process was employed to prepare an acrylate copolymer emulsion, Latex D, from monomer having the same

composition but which is believed to result in an emulsion polymer having a substantially lower proportion of acid functionality at the polymer surface. Latex D contained 44.6% solids with an average particle diameter of 158 nm.

A tinted titanium dioxide pre-dispersion in which the dispersant (Tamol SG-1 dispersant) level was 1% (on titanium dioxide) was prepared according to the following formulation.

<u>Component</u>	<u>Weight (g)</u>
water	169.9
Nopco NXZ defoamer	3.0
Tamol SG-1(35%) dispersant	17.1
Ti-Pure R-900 titanium dioxide	600

The pigment grind components were milled on a high speed disk disperser (Laboratory Dispersator, Model 84, Premier Mill Corp.) at 3000 rpm for 20 minutes. At a lower speed 30.0 g of Colortrend111 (trademark of Tenneco Inc.) 888-9907 B-Lamp Black was mixed in.

To 62.9 g of the tinted pre-dispersion was added with stirring 169.4 g of Latex C binder (preadjusted to pH 6.0 with 28% aqueous ammonia) and 9.3 g of water. To 120.8 g of the resulting mixture was added 5.2 g Texanol coalescent, 7.2 g propylene glycol, and 24.0 g of a 2.5% aqueous solution of Natrosol 250 MR. The final pH of this mixture was adjusted to 7.5 with 28% aqueous ammonia to yield a paint (Example 106) with 14% volume concentration of titanium dioxide in the dry paint and a volume solids content of ca. 30% in the wet paint.

The above procedure was repeated using 169.7 g of Latex D binder (preadjusted to pH 6.0) instead of Latex C and 9.0 g of water to form an analogous paint (Example 107).

A tinted pigment dispersion was prepared as in Example 106 except that 17.3 g of Tamol 963 dispersant (35%) (sodium salt of polyacrylic acid) instead of Tamol SG-1 dispersant was used to give a one percent Tamol 963 dispersion.

The paint formulation process of Example 106 was repeated substituting the

Tamol 963 pigment dispersion for the Tamol SG-1 pigment dispersion using Latex C to provide Comparative Example 24 and Latex D to provide Comparative Example 25. After four days the paints were evaluated for latex adsorption and for differences in titanium dioxide scattering efficiency. Adsorption was measured by diluting one part of the paint with seven parts by weight of water, centrifuging, and determining the concentration of the unadsorbed latex in the supernatant gravimetrically.

The relative scattering was determined by measuring the Y-reflectance of the tinted paints with a 45°/0° reflectometer (Colorguard, Gardner Instruments). From light scattering theory, the ratio of the scattering coefficient, S, and the adsorption coefficient, K, is given by:

$$S/K = 2R/(1-R)^2$$

where R is the reflectance from an infinitely thick layer of dry paint film. At a given titanium dioxide PVC, differences in Y-reflectance of equally tinted paint films arise solely from differences in titanium dioxide scattering efficiency. Titanium dioxide dominates the scattering while the tinting agent dominates the adsorption which can then be considered constant. The percentage difference in scattering coefficient exhibited by two equally tinted paints is then given by:

$$((S_2 - S_1)/S_1) \times 100 = ((R_2(1 - R_1)^2/R_1(1 - R_2)^2) - 1) \times 100$$

Results are given in Table III. The results in Table III show that the Latex C polymeric binder (Example 11) provides substantially higher adsorption on titanium dioxide than does the Latex D polymeric binder (Example 12). The difference in Y-reflectance represents 48% higher scatter from the titanium dioxide. This result demonstrates the advantage of a high acid functionality at the latex particle surface on the adsorption process of this invention. High surface acid functionality is believed to promote adsorption to titanium dioxide thereby enhancing the ability of the latex binder to compete with the

polyelectrolyte dispersant for the titanium dioxide surface. The results for Comparative Examples 4 and 5 show no difference between the two in adsorption and essentially no difference in Y- reflectance.

Comparison of the results for Example 11 and Comparative Example 4 show that the dispersant employed to prepare the titanium dioxide pre-dispersion has a significant effect on the adsorption of the polymeric latex dispersant Latex C with high surface acid functionality. When the polyelectrolyte Tamol 963 dispersant was employed, it was not displaced from the surface of the titanium dioxide particles to permit adsorption of the polymeric Latex C. However, this same polymeric latex was effective to displace the Tamol SG-1 dispersant, which has a lower proportion of acid functionality on a weight basis than the Tamol 963 dispersant and is believed to be more weakly bound to the titanium dioxide surface.

Table\_III

<u>Example</u>	<u>Latex</u>	<u>Dispersant</u>	<u>Adsorption</u>	
			<u>(mg/g)</u>	<u>Y-Reflectance</u>
11	C	1% Tamol SG-1	720	0.557
12	D	1% Tamol SG-1	110	0.492
C. 41	C	1% Tamol 963	50	0.544
C. 51	D	1% Tamol 963	50	0.541

-----

#### 1. Comparative example.

##### Example\_108

A multi-stage gradual addition process was employed to prepare an acrylate copolymer emulsion from monomer including about 2.5 percent by weight methacrylic acid. The polymeric latex, Latex E, contained 44.5% solids with an average particle diameter of 150 nm, and was prepared by a process believed to provide a substantial proportion of acid functionality at the surface of the latex

particle as determined by potentiometric titration. A modification of the process was employed to prepare an acrylate copolymer emulsion, Latex F, from monomer having the same composition, but which is believed to result in an emulsion polymer having a substantially lower proportion of acid functionality at the polymer surface. The latex, Latex F, contained 44.8% solids with an average particle diameter of 159 nm.

To 86.1 of Latex E (preadjusted to pH 9.0 with aqueous ammonia) was added 31.5 g of a titanium dioxide-Tamol SG-1 dispersion prepared as in Examples 106-107, 3.3 g of deionized water, 1.9 g of Texanol coalescent, 7.2 g of propylene glycol, and 24.0 g of a 2.5% aqueous solution of Natrosol 250 MR. These ingredients were well mixed to yield a paint (Example 108) with 14% PVC of titanium dioxide and volume solids of ca. 30%.

To 85.2 g of Latex F (preadjusted to pH 9.0 with aqueous ammonia) was added 31.5 g of the same titanium dioxide-Tamol SG-1 dispersion, 6.2 g of deionized water, 1.9 g of Texanol coalescent, 7.2 g of propylene glycol, and 24.0 g of a 2.5% aqueous solution of Natrosol 250 MR. These ingredients were well mixed to yield a paint (Comparative Example 26) with 14% PVC of titanium dioxide and volume solids of ca. 30%.

Example 108 and Comparative Example 26 were evaluated for polymeric latex adsorption after one hour, one day, and five days of equilibration. Both paints were also evaluated for Y-Reflectance after one day and nine days of equilibration in the same manner as Examples 106 - 107. The results are given in Table XVII.

Table XVII

<u>Example</u>	<u>Latex</u>	<u>Adsorption (g/g TiO<sub>2</sub>)</u>			<u>Y-Reflectance</u>	
		<u>1hour</u>	<u>1day</u>	<u>5days</u>	<u>1day</u>	<u>9days</u>
108	E	0.01	0.17	0.23	0.530	0.536
Comp. 261	F	-0.05	-0.09	-0.03	0.502	0.498

1. Comparative example.



These results demonstrate that a polymeric latex with high acid functionality at the latex particle surface, such as Latex E, the adsorption process is not instantaneous but occurs over the time scale of days. After one day a paint prepared with a high surface acid functionality polymeric latex binder, Latex E, had 18.5% higher light scatter than a paint prepared with a low surface acid functionality polymeric latex, Latex F. After nine days this difference increased to 26%.

#### Example 109

To 1300 g of deionized water stirred under a nitrogen atmosphere at 85°C was added 4 g of ammonium persulfate in 24 g of deionized water and 60 g of a seed latex. A monomer emulsion prepared from 600 g of deionized water, 28 g of Siponate DS-4, 900 g of butyl acrylate, 876.6 g of methyl methacrylate and 23.4 g of methacrylic acid was added over a 200-min period along with 2 g of ammonium persulfate in 100 g of deionized water maintaining 85°C. When the reaction was complete, the dispersion was cooled and filtered. The product (Latex G) had 45.6% solids and pH 3 with an average diameter of 196 nm.

The process used to prepare Latex G was repeated, except that 18 g of the methyl methacrylate was replaced with an equal weight of Kayamer115 (trademark of Nihon Kayaku Co. Ltd.) PM-1 (monomer mixture containing around 52% of the monoester of hydroxyethyl methacrylate and phosphoric acid and 33% of the diester). The product (Latex H) had 46.1% solids and pH 2.6 with an average particle size of 185 nm.

A tinted titanium dioxide dispersion was prepared as in Examples 106-107 from 180 g of deionized water, 7.2 g of Tamol 731 dispersant (25% solids), 3.0 g of Nopco NXZ defoamer, 600 g of Ti-Pure R-902 and 30 g of Colortrend lamp black dispersion. Samples of Latex G and Latex H were adjusted to pH 9 with 28% aqueous ammonia and used to formulate paints with 14% volume concentration of Ti-Pure R-902 pigment in the dry paint: To 29.5 g of R-902 dispersion was added 7.8 g of water, 83.9 g of the pH 9 Latex G, 2.6 g of Texanol coalescent, 7.2 g of propylene glycol and 24.0 g of 2.5% aqueous Natrosol 250 MR hydroxyethyl cellulose thickener. Latex H was formulated similarly only 82.8 g were required

and 8.9 g of water. The two paints were allowed to equilibrate for seven days and then the adsorption of polymeric latex on titanium dioxide in the paints and their Y-reflectance was measured as above. The results are given in Table XVIII.

Table XVIII

Example	Latex	Adsorption (g/g TiO <sub>2</sub> )	Y-Reflectance
Comp. 271	G	0.01	0.504
109	H	0.26	0.540

---

#### 1. Comparative example

These results show that the standard binder (Latex G) is essentially non-adsorbing under these conditions. The phosphate-containing binder (Latex H) adsorbs substantially and the increased Y-reflectance that accompanies the adsorption corresponds to an increase in scattering efficiency of the titanium dioxide in the dry paint film of 25%.

#### Example 110

Polyelectrolyte is typically used as pigment dispersant in latex paint formulation. The elimination of this water sensitive dispersant in polymeric latex-adsorbed pigment dispersions is expected to improve coating water and corrosive resistances. Moreover, the process of the present invention provides films with more homogeneous pigment distribution than prior art processes. The improved pigment distribution is believed to block channels for transporting ion and water to the coating-steel interface.

Maincoat116 HG-54 polymeric latex (Maincoat is a trademark of Rohm and Haas company), a commercially available latex intended for industrial coatings applications, was ground with titanium dioxide in the absence of polyelectrolyte dispersant to prepare a latex-dispersed paint (Example 110) according to the

following formulation: The following ingredients were ground at 3000 rpm for 15 minutes using a Cowles Dissolver: (All ingredients are parts by weight)

	<u>Example 110</u>	<u>Comparative Example 28</u>
methyl Carbitol		
wet edge agent	17	17
Tamol 165 (21%) dispersant	0	4
Triton CF-10 wetting agent	0	1
Foamaster DS antifoamer	1	1
Ti-Pure R-900 titanium dioxide	85	85
Maincote HG-54 polymer latex (41.5%, preadjust to pH = 9)	275.2	0
The pigment grind is let down with: deionized water (preadjust to pH = 9)	65.6	61.2
mixture of (30 part Propasol P, 60 part butyl Carbitol, and 12 parts Acrysol RM-825 thickener (25%))	34	34
Maincote HG-54 polymer latex (41.5%, preadjust to pH = 9)	0	275.2
NH <sub>4</sub> OH (28%)	1.75	1.75
Texanol coalescent	17.15	17.15
sodium nitrite (15%)		
flash rust inhibitor	4.5	4.5

Samples of the paints of Example 110 and comparative Example 28 were drawdown on Bonderite 117 B-1000-treated (trademark of Parker Chemical Co.) steel panels, and dried at 77° F, 50% humidity for 3 weeks. The dry film thickness

was 1 mil. The dry panels were then put in salt spray chamber (100° F, 5% NaCl) for 1 week. Performance results are given in Table XIX. Latex-dispersed titanium dioxide paint (Example 110) had less rust spread out from scribed marks than conventionally dispersed titanium dioxide paint (Comparative Example 28).

Table XVIII

<u>Example</u>	<u>Inches rust spread from scribe</u>
110	3/8
Comp. Ex. 28 <sup>1</sup>	5/8

1. Comparative example.

## Example 111

An acid-free acrylic polymer latex having a calculated Tg of about 0°C and a particle size of 141 nm was prepared via a conventional gradual-addition, batch polymerization process using a nonionic peroxide/reducing agent initiator system and a nonionic ethoxylated nonylphenol surfactant. Included in the monomer mixture used in the copolymerization was 6% of a methacrylate monomer having a  $\text{CH}_3(\text{CH}_2\text{CH}_2\text{O})_{45}$  pendant group. This provides a surface layer of water-soluble polymer around each latex particle which acts as a steric barrier to stabilize the latex against aggregation.

The process of Example 1 was repeated using this latex. Grinding conditions were: pH = 9, PVC = 30%, volume solids = 38% and mg Latex added per g  $\text{TiO}_2$  = 654. Adsorption was measured as in Example 1 and was found to be 93 mg/g after 1 day and 123 mg/g after 1 week. This example illustrates the adsorption process of the present invention employing latex particles which are sterically stabilized.

Examples 201a -201f

Calcium carbonate is widely used as an extender pigment or filler for polymeric latex compositions for a wide variety of applications including mastics, caulks, coatings, and others. One natural ground, widely used, grade of calcium carbonate, Atomite (trademark of Thompson, Weinman & Co.), has particles which are positively charged in the alkaline pH range, and is frequently employed in polymeric latex compositions. Compositions including calcium carbonate pigment are usually treated with a small amount of anionic polyelectrolyte dispersing agent in order to avoid gross aggregation of the polymeric latex with the pigment.

Different amounts of a polyacrylic acid dispersant were added to an aqueous dispersion of Atomite calcium carbonate particles (202.5 g calcium carbonate in 204.3 g DI water, adjusted pH to 9 with acetic anhydride). The suspension was sheared at approximately 3000 rpm for 15 minutes and then was added to 363.2 g of an acrylic polymeric latex (98 BA/2 MAA, 0.5 micron particle size, 53% solids, preadjusted pH to 9) and sheared for 15 minutes, to provide the composite particles of Examples 201a-201f illustrating the effect of adsorbed polyelectrolyte dispersant on adsorption of polymeric latex particles on the inorganic material particles.

The samples were observed visually for grit formation and latex adsorption was calculated from gravimetric determination of latex concentration in supernatant after samples were centrifuged at 1000 rpm for 2 hours. The results are shown below in Table LI.

Table LI

Example	C.201 <sup>1</sup>	201a	201b	201c	201d	201e	201f
% poly AA <sup>2</sup> on CaCO <sub>3</sub>	0	0.025	0.035	0.050	0.100	0.150	0.200
Adsorption (mg/g CaCO <sub>3</sub> )	250	720	630	460	320	190	75
Grit	severe	none	none	none	none	none	none

- 
1. Comparative example
  2. Polyacrylic acid

The results given in Table LI show that simply mixing calcium carbonate with polymeric latex results in severe grit formation, attributable to instability (Comparative Example 201). On the other hand, if too much polyelectrolyte dispersant is added, adsorption of polymeric latex on the inorganic material pigment is severely reduced.

### Examples 202 - 203

Natural ground silica, Imsil (trademark of Illinois Minerals Co.) A-10 silica (two micron mean particle size) has a large negative surface charge density (zeta potential of about -60 mv at pH = 9) in basic aqueous media. As shown in Table LII, when an acrylic polymeric latex is mixed with a suspension of Imsil A-10 silica (at 30 percent pigment volume content, 37 percent total volume solids) at pH = 9.0, no adsorption of the polymeric latex particles onto the surface of the silica takes place (Comparative Example 202). However, when the silica is treated with an aminosilane to reduce the effective surface potential of the silica, substantial adsorption of the acrylic polymeric latex occurs (Examples 202, 203a-203c). The data in Table II also show that the adsorption is pH-dependent, as the pH is increased above 9.0, adsorption decreases (Example 203c) and does not occur at all at pH = 10.0 (Comparative Example 203). Similarly, below pH = 8.0, the stability of the dispersion of composite particles declines, as reflected by the increase in observed grit at pH = 8.0.

Table LII

Example	C.202 <sup>2</sup>	202	203a	203b	203c	C.203 <sup>2</sup>
pH	9.0	9.0	8.0	8.5	9.5	10.0
% aminosilane <sup>1</sup> on silica	none	0.013	0.013	0.013	0.013	0.013
adsorption (mg/g)	-75	685	390	580	75	-75
grit	none	none	trace	none	none	none

1. Aminosilane:  $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$

2. Comparative example.

Examples 204 - 206

Pressure sensitive adhesives ("PSA") based on polymeric latex typically do not contain inorganic extender pigments. Although including low cost extender pigments would result in reducing the raw material costs of manufacturing pressure sensitive adhesives, the use of conventional methods to disperse extender pigments in polymeric latex PSA results in a substantial decrease in PSA properties, especially peel resistance and tack.

In order to induce the adsorption on silica of a PSA polymeric latex (98 BA/ 2 MAA, 0.5 micron particle size, 53 percent by weight solids) which has a negative charge on the surface of the polymeric latex particles, albeit at a lower level than the Imsil A-10 natural ground silica (zeta potential of about -80 mv at pH of 9), the silica was treated with Dow Corning Z-6020 aminosilane (aminoethylamino-propyltrimethoxysilane) to lower the negative charge density of silica surface. The amount of Z-6020 silane was empirically determined by running concentration ladders to give good polymeric latex adsorption without gross aggregation of the polymeric latex with silica to provide Examples 204-206. Comparative examples 204-205 have the same composition, except Tamol (trademark of Rohm and Haas Co.) 731 polyelectrolyte was used as the dispersant for the silica. Examples 204-206 differ in the ratio of silica to polymeric latex.

The latex-dispersed silica was prepared as follows: The following ingredients were ground at 3000 rpm for 15 minutes using a Cowles dissolver to provide a treated silica suspension with a less negative surface potential:

<u>Component</u>	<u>Parts by Weight</u>
Imsil A-10 silica	324
deionized water	215.8
NH <sub>4</sub> OH (28%)	(to pH = 9)
mixture of (3 parts Dow Corning Z-6020, 1.25 part acetic acid, and 18 part water)	2.4

Differing ratios of the treated silica suspension were added with mechanical stirring to the polymeric latex (pH preadjusted to 9) along with additional water to adjust the solids level and defoamer as follows to provide pressure sensitive adhesives dispersed with polymeric latex (Examples 204-206):

<u>Example</u>	<u>204</u>	<u>205</u>	<u>206</u>
silica suspension	45	90	135
deionized water	16.4	8.2	0
polymeric latex	186.8	166.0	145.3
Bubble Breaker	0.19	0.17	0.15
3056A antifoamer			

A series of comparative examples in which the silica was dispersed by a conventional polyelectrolyte dispersant were prepared as follows: The following ingredients were ground at 3000 rpm for 15 minutes using a Cowles dissolver to provide conventional dispersions of silica:

Parts by Weight

Imsil A-10 silica	324
deionized water	115
NH <sub>4</sub> OH (28%)	(to pH = 9)
Tamol 731 (25%) dispersant	12.96

Pressure sensitive dispersions were then prepared by adding the conventionally dispersed silica to the polymeric latex in differing ratios with mechanical stirring as follows:

<u>Comparative Example</u>	<u>204</u>	<u>205</u>
silica dispersion	45	135
deionized water	37.4	34.2
polymeric latex	223.1	173.7
Bubble Breaker 3056A	0.19	0.15
antifoamer		



Optical microscopy showed that samples of the pressure sensitive adhesives of Examples 204-206 had latex-adsorbed on the surface of the silica particles, while samples of the pressure sensitive adhesives of Comparative Examples did not have any latex associated with silica.

Samples of the silica-filled pressure sensitive adhesives were coated to the treated side of 1.2 mil polypropylene film, and dried 5 minutes at 70°C to give a final adhesive thickness of 1 mil. The performance of those adhesives on a stainless steel surface is reported in Table LIII. These results show that the latex-dispersed silica adhesives show better peel, shear and tack, especially at higher filler loading. The latex-adsorbed silica is believed to provide better pressure sensitive adhesive properties due to better extender distribution in the adhesive film and because it is believed that no uncoated silica particles are likely to protrude from the surface of the adhesive.

Table LIII

<u>Adhesives</u>	<u>Peel<sup>2</sup></u> <u>PVC<sup>1</sup></u>	<u>Shear<sup>3</sup></u> <u>(oz/in)</u>	<u>Polyken<sup>4</sup></u> <u>(hours)</u>	<u>Finger<sup>5</sup></u> <u>Tack</u>	<u>Tack</u>
Example 204	10	24	2.3	540	V.Good
Comparative Example 204	10	18	2.8	520	V.Good
Example 205	20	20	4.3	480	Good
Example 206	30	11	8.8	250	Fair
Comparative Example 205	30	3	4.2	90	Poor

1. Calculated silica volume content in dry adhesive
2. Peel adhesion was measured with an Instron Universal Testing Instrument, Model 1122 equipped with a Microcon I, and employing a dwell time of one minute and a crosshead speed of 12 inches per minute.
3. Shear adhesion was measured as by the time required for a test strip adhered to a steel plate with a one-half inch by one inch rectangle of adhesive and

suspending a one kilogram weight to fall from the steel substrate.

4. Polyken tack was measured using a Polyken Probe Tack Tester Series 400 tester (Testing Machines Inc.) using a dwell time of one sec, a speed of one centimeter per second, and an applied pressure of 100 grams per square centimeter.
5. Finger tack was rated qualitatively.

#### Examples 207 - 209

In the following examples, a small amount (0.05% percent by weight on calcium carbonate solids) of anionic polyelectrolyte dispersant, Tamol 850 dispersant, was used to provide a negative charge on the surface of the calcium carbonate particles. At this level of anionic dispersant, the calcium carbonate particles could be dispersed with a polymeric latex (0.35 micron particle size, zeta potential = -80 mv) to give stable latex-adsorbed calcium carbonate particle dispersions (Examples 207-209), as observed by optical microscopy. In contrast, at a higher level of anionic dispersant (0.4 percent by weight of calcium carbonate), the calcium carbonate dispersions were found to be stable, but without polymeric latex particles adsorbed to the surfaces of the calcium carbonate particles.

Latex-adsorbed calcium carbonate dispersions were prepared as follows: The following ingredients were ground at 3000 rpm for 15 minutes using a Cowles dissolver (all ingredients are parts by weight):

Example	207	208	209
Atomite calcium carbonate	50.1	94.5	121.5
deionized water	18.5	41.5	50.5
NH <sub>4</sub> OH (28%)	(to pH = 9)	(to pH = 9)	(to pH = 9)
Tamol 850 (30%) dispresant	0.084	0.158	0.203
Nopco NXZ antifoam	0.3	0.3	0.3

The resulting dispersions were added to the following ingredients under stirring:

125

Polymeric latex (55% solids)	144.6	130	110
NH <sub>4</sub> OH (28%)	(to pH = 9)	(to pH = 9)	(to pH = 9)
Nopco NXZ antifoam	0.3	0.3	0.3
Natrosol 250 MXR thickener (10% in propylene glycol)	6.0	7.5	8.0

The ratio of calcium carbonate to polymeric latex solids were selected to provide the following calcium carbonate volume contents in dry films:

Example:	207	208	209
CaCO <sub>3</sub> volume content in dry films	20	35	45

In addition, a series of conventionally dispersed compositions (Comparative Examples 206-208) were prepared by increasing the level of anionic polyelectrolyte dispersant by a factor of eight.

Films of samples of Examples 207-209 and Comparative Examples 6-8 were cast and allowed to dry for 3 weeks at 77 F 50% relative humidity. The final dry film thickness is approximately 20 mil. The mechanical properties of those calcium carbonate-filled polymeric latex films are given in Table LIV.

The results in Table LIV show that latex-dispersed calcium carbonate films show much lower modulus together with improved stress, elongation and toughness, especially at higher filler loading, than films formed from conventionally dispersed calcium carbonate-filled polymeric compositions. The improved mechanical properties are believed to result from the reduction or elimination of the probability of pigment-pigment contact during film drying, thus creating a film with more homogeneous pigment distribution, and better film elongation and properties more similar to those of the polymer itself. As a corollary, it is expected that the process of the present invention will permit the use of higher contents of inexpensive filler, such as calcium carbonate, to be incorporated in polymeric latex compositions, with less attrition of film mechanical properties such as modulus and toughness.

Table LIV

<u>Example</u>	<u>PVC</u> <sup>2</sup>	<u>Maximum Stress (psi)</u> <sup>3</sup>	<u>%Elong.</u> <sup>3</sup>	<u>Modulus</u> <sup>3</sup> <u>(psi)</u>	<u>Toughness</u> <sup>3</sup> <u>(psi)</u>
207	20	140	710	31	650
Comp. 206 <sup>1</sup>	20	145	755	34	710
208	35	185	465	180	620
Comp. 207 <sup>1</sup>	35	150	330	380	380
209	45	205	250	360	360
Comp. 208 <sup>1</sup>	45	165	165	1600	235

1. Comparative example.
2. Volume concentration of calcium carbonate.
3. Maximum stress, percent elongation, modulus, and toughness were measured using a Model 1122 Instron Universal Testing Machine using a gauge length of 1.0 inch and a crosshead speed of 2 inches per minute.

Example 210

Clay is used as a filler in paper coating. Because the structure of clay is that of a platelet, the clay particles tend to align themselves to create undesirably high gloss in a paper coatings. Clay has a surface charge on its basal planar surfaces which is similar to silica. In order to prepare latex-dispersed clay particles, Hydrafine (trademark of I.M. Huber Co.) clay particles (0.7 micron particle size) were treated with a small amount of amino-functional silane (Dow Corning Z-6020) as follows:

The following ingredients were ground at 3000 rpm for 15 minutes using a Cowles dissolver:

	<u>Parts by Weight</u>
Hydrafine clay	100
deionized water	44.3
NH <sub>4</sub> OH (28%)	(to pH = 9)
mixture of (3 part Dow Corning Z-6020, 1.25 part acetic acid and 18 part water)	0.82

The resulting suspension was added to 46.05 parts by weight of Rhoplex (trademark of Rohm and Haas Co.) B-15 polymeric latex, a commercially available binder for paper coatings ((0.15 micron particle size, preadjusted to pH 9, 39.1% solids) under stirring for 5 minutes, then the pH was dropped to 7 with acetic anhydride to provide a paper coating composition (Example 210). This formulation provides 18 parts of polymeric latex solids on 100 parts of clay.

This process was repeated except that 0.1 parts by weight of Calgon (trademark of Calgon Corp.) RS-1 pigment dispersant (polyphosphate) was used instead of 0.82 parts by weight of Dow Corning Z-6020 mixture (Comparative Example 209).

The Rhoplex B-15 polymeric latex particles are too small to be clearly seen with optical microscopy. Hence, the amount of latex adsorbed on clay was determined by gravimetric analyses of latex concentration in supernatant after samples were centrifuged at 1000 rpm for 2 hours, and the results are reported in Table LV below:

Table LV

Latex adsorption (mg B-15/g clay)

Example 210	64
Comparative Example 209	-2

Samples of the paper coatings of Example 210 and Comparative Example 209 were coated on paper and on cardboard to equal weight applied with a wire wound rod. The coatings were permitted to dry for one minute at 180 F, and their performance properties were evaluated. The results of the evaluation is reported in Table LVI. These results show that the latex-dispersed clay coating has lower gloss on both paper and cardboard substrates, and also is a smoother, higher strength (lower wet pick) coating on paper.

Table LVI

	<u>Gloss<sup>2</sup></u>	<u>Gloss after Calendered<sup>3</sup></u>	<u>Smooth<sup>4</sup></u>	<u>Wet Pick<sup>5</sup></u>
<u>Coating on Paper</u>				
Example 210.	19.3	50.1	1.7	3.3
Comp. 209 <sup>1</sup>	24.8	53.6	2.2	3.7
<u>Coating on Cardboard</u>				
Example 210	21.0	58.9	3.5	4.0
Comp. 209 <sup>1</sup>	30.5	63.4	2.8	3.0

1. Comparative example.
2. Gloss was measured at 75°C.
3. Calendering was performed on paper using one pass at 500 feet per minute at 200 F and 600 psi. Calendering was performed on cardboard using one pass at 500 feet per minute at 250 F at 300 psi.
4. Smoothness was measured by air flow over the surface, and ranked on a scale of 1 to 4, with the 1 being best.
5. Wet pick was measured by applying a 20% aqueous isopropanol solution to the coated stock using a roller to wet the stock and subsequently evaluating the pick resistance qualitatively on a scale of 1 to 4.

Examples 211 - 212

Rhoplex TR-407 (T<sub>g</sub> = 30 C, 0.25 micron particle size, 45.5 percent solids) polymeric latex is used commercially to bind fibers. In such applications, filler pigment is not typically used, because conventional methods employed to disperse inorganic filler materials in polymeric latex binders result in poor fiberfill performance.

Two different filler materials, Albaglos (trademark of Pfizer Corp.) calcium carbonate (0.75 micron particle size) and Hydrafine clay, were dispersed with

polymeric latex using the process of the present invention. In the case of Albaglos calcium carbonate it was not necessary to add even a small amount of anionic polyelectrolyte to obtain a stable latex-adsorbed Albaglos calcium carbonate dispersion. Polymeric latex-dispersed inorganic particle dispersions were prepared as follows:

The following ingredients were ground at 3000 rpm for 15 minutes using a Cowles dissolver (all ingredients are parts by weight):

Example	211	212
Albaglos calcium carbonate	600	0
Hydrafine clay	0	600
deionized water	415.6	415.6
NH <sub>4</sub> OH (28%)	(to pH = 9)	(to pH = 9)
Mixture of (3 part Dow Corning Z-6020, 1.25 part acetic acid, and 18 part water)	0	4.11

To each of the resulting dispersions were added 1318.7 parts by weight of Rhoplex TR-407 polymeric latex (preadjusted pH to 9) under stirring for 5 minutes, providing fiberfill coating materials (Examples 211 and 212) having 100 parts of polymeric latex solids on 100 parts of filler.

The dispersion processes were repeated except that 8.01 parts by weight of Tamol 850 (30% solids) polyelectrolyte dispersant was used for both fillers instead of none for Albaglos and 4.11 parts by weight of the Dow Corning Z-6020 silane mixture for Hydrafine clay to give Comparative Examples 210 and 211.

Samples of the fiberfill binders were sprayed on polyester fiber at fiber/polymeric latex solids = 100/15 by weight, and were dried and cured at 150 C for 5 minutes. The performance of the fiberfill binders was evaluated and is reported in Table LIV. These results show that polymeric latex-dispersed fiberfill binders show better washability, wet and dry tensile strength than the respective conventionally dispersed binders.

Table LVI

<u>Example</u>	<u>Washability</u> <sup>2</sup>	<u>Tensile Strength (psi)</u>	
		<u>Dry</u> <sup>3</sup>	<u>Wet</u> <sup>4</sup>
211	1.5	695	115
Comp. 210 <sup>1</sup>	1.0	570	40
212	4.5	935	440
Comp. 211 <sup>1</sup>	3.7	705	130

1. Comparative example.
2. Washability was measured using Dacron 371W fibers (not heat-bonded) as polyester fiber, and washing in a washing machine (full cycle, 50 - 60°C hot water, one-half cup Pennico Plus industrial detergent) and ranked 1 - 5 qualitatively (5 best).
3. Dry and wet tensile strength was measured according to ASTM D-1117 (4 inch gauge, 300 %/minute). For wet tensile the sample is soaked for 30 minutes in water containing 0.1 percent by weight Triton X-100 surfactant.

Examples 213 - 215

Example 212 and Comparative Example 211 were repeated, except that one percent on solids of anionic surfactant was subsequently added to each, and the dispersions were then frothed to a density of 0.08 gm/cc and coated on one side of the air laid non-woven batt using a padder (one nip, no external pressure on the roll) to give Example 213 and Comparative Example 212. Add-on was at 2.6 oz/sq. yd. A subjective hand analysis was made on the finished samples to determine their relative firmness and showed that Example 213 was firmer than Comparative Example 12.

The process of Example 213 was again repeated except that instead of treatment with the aminosilane the clay was treated either by addition of aluminum sulfate or the pH was lowered by addition of glacial acetic acid as follows to give Examples 214 and 215 respectively.



The following ingredients were added in order with good agitation:

	<u>Example 214</u>	<u>Example 215</u>
Hydrafine clay	50	50
DI water	. . . . .25.0	27.26
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .16-18 H <sub>2</sub> O	. . . . .0.61*	
DI water	. . . . .9.39*	
Rhoplex TR-407 (45.5% solids)	. . . . .109.89*	109.89
glacial acetic acid	. . . . .-	7.74

\*Premix

The adsorption of polymeric latex on clay in Examples 213, 214, and 215 and the lack of polymeric latex adsorption in Comparative Example 212 were observed from optical microscopy. The amount of latex adsorbed on clay was measured through gravimetric analyses of latex concentration in supernatant after samples were centrifuged at 1000 rpm for 2 hours; the results are shown below in Table LVII.

Table LVII

Latex adsorption (mg TR-407/g clay)

Example 213	385
Example 214	260
Example 215	305
Comparative Example 212	50

A subjective hand analysis was made on the finished samples to determine their relative hardness. It was found that the sample of Example 214 was harder than the sample of Comparative Example 212. These results show the superior adsorption obtainable on clay particles using the process of the present invention.

## Examples\_301-303

A typical conventionally dispersed 20% PVC gloss paint (Comparative Example 301) was prepared according to the following formulation.

Pigment grind:

Components	Weight_(g)
water	30.0
propylene glycol	20.0
Colloid 643 defoamer	1.0
Tamol 731 dispersant (25% solids)	8.19
Ti-Pure R-900 titanium dioxide	204.72

Tamol 731 is a polycarboxylate dispersant (Tamol is a trademark of Rohm and Haas Company). Tamol 731 is a sodium salt of polymeric carboxylic acid. Pigment dispersion with one percent by weight polymeric carboxylic acid dispersant as in this case is considered conventional. Ti-Pure is a trademark of Du Pont de Nemours Co. Ti-Pure R-900 is a coatings grade of rutile titanium dioxide. These components were milled on a high speed disk disperser to form a pigment grind, and were let down at a slower speed with the following:

Components	Weight_(g)
Rhoplex AC-61 polymer latex	493.75
Colloid 643 defoamer	4.0
Texanol coalescent	22.96
Triton GR-7M surfactant	2.0
propylene glycol	59.0
Nuosept 95 preservative	6.0
water and Natrosol 250 MR	165.07
cellulosic thickener	

Rhoplex is a trademark of Rohm and Haas Company. Texanol is a trademark of Eastman Kodak Co. Triton is a trademark of Rohm and Haas Company.

Nuosept is a trademark of Nuodex, Inc. The mix is thickened to a Stormer viscosity of 80 KU by addition of an aqueous solution of the cellulosic thickener, and the pH of the mix is adjusted to 9 by addition of ammonia.

To provide Example 301, the paint formulation process of Comparative Example 301 was repeated replacing the 493.75 g of Rhoplex AC-61 with a mixture of 419.66 g Rhoplex AC-61 (46.5% solids) and 92.04 g of a polymeric latex having a glass transition temperature of 65°C, a particle size of 71 nm, and having 6% phosphoethyl methacrylate (Latex A, 37.4% solids). The total weight of water was adjusted to maintain the same total solids in the final paint.

The paint formulation process of Example 301 was repeated with the 1% Tamol 731 decreased to 0.5% to give Example 302.

The paint formulation process of Example 301 was repeated substituting Tamol SG-1 for Tamol 731 to give Example 303.

For each paint, a sample was removed just before addition of the cellulosic thickener, allowed to equilibrate for two hours, diluted 1 part to 3 parts with water, and centrifuged. The concentration of unadsorbed latex in the supernatant was determined gravimetrically and used to calculate the milligrams of latex adsorbed per gram of titanium dioxide.

Kubelka-Munk scattering coefficients were determined for all paints using a modification of ASTM D 2805-70.

The results are given in Table CI.

Table CI

..... Adsorption . Scattering				
Example	Dispersant	Binder__	__(mg/g)_. Coefficient__	
Comp. 301	1% Tamol 731	AC-61	3	7.26
301	1% Tamol 731	AC-61/Latex A	199	7.77
302	0.5% Tamol 731	AC-61/Latex A	200	8.18
303	1% Tamol SG-1	AC-61/Latex A	225	8.27

The results for Example 301 in Table CI demonstrate that a polymeric latex with high acid functionality at the latex particle surface when blended with a conventional latex will preferentially adsorb on titanium dioxide under conditions where the conventional latex will not adsorb. Thus Comparative Example 301 shows that Rhoplex AC-61 does not adsorb on titanium dioxide in the presence of 1% Tamol 731 while Example 301 shows that a blend of Latex A with Rhoplex AC-61 provides substantial adsorption and increased hiding as reflected by the Kubelka-Munk scattering coefficients. The latex adsorption of 199 mg/g measured for Example 301 is close to value of 169 mg/g measured independently for Latex A in the absence of Rhoplex AC-61 and is significantly below the value of about 400 mg/g measured independently for Rhoplex AC-61. The lower adsorption observed for Latex A is consistent with its smaller 71 nm particle size compared to the 150 nm Rhoplex AC-61.

Comparison of the results for Examples 302 and 303 with those for Example 301 shows that amount and type of dispersant used to prepare the titanium dioxide pre-disposed has a significant effect on the behavior of the paint made by letting down this pre-dispersion with a blend of Rhoplex AC-61 and polymeric Latex A. Either decreasing the amount of Tamol 731 (Example 2) or replacing the Tamol 731 with Tamol SG-1, which has a lower proportion of acid functionality and is believed to be more weakly bound to the titanium dioxide surface (Example 303), provides greater adsorption and increased hiding.

#### Example\_304

A typical conventionally dispersed pigment grind containing one percent Tamol SG-1 polymeric carboxylic acid dispersant by weight on pigment was prepared according to the following formulation:

135

Components	Weight_(g)
water	. . . . . 70.0
propylene glycol	. . . . . 20.0
Colloid 643 defoamer	. . . . 1.0
Tamol SG-1 dispersant (35% solids)	5.85
Ti-Pure R-900 titanium dioxide	. . . 204.72

These components were milled on a high speed disk disperser to form a pigment grind. 237.6 g of a 120 nm polymeric latex (38.0% solids) prepared using a gradual-addition, batch process and having a monomer composition of 5 BA/93 MMA/2 MAA was then added and the mixture milled for 15 minutes to give Comparative Example 302.

After equilibrating for 1 hour, a sample was removed, diluted 1 part to 3 parts with water, and centrifuged. The concentration of unadsorbed latex in the supernatant was determined gravimetrically and used to calculate the milligrams of latex adsorbed per gram of titanium dioxide. The resulting value for Comparative Example 302 was 25 mg/g.

Example 304 was prepared in the same manner using 239.5 g of a 127 nm polymeric latex (37.7% solids) prepared using a gradual addition, batch process and having a monomer composition of 5 BA/89 MMA/2 MAA/4 phosphoethyl methacrylate. The measured adsorption for Example 304 was 219 mg/g.

A portion of each grind was diluted to about one percent by volume with water, a small drop placed on a standard SEM sample holder, and the water allowed to evaporate. The dried samples were then sputter coated with gold and examined via scanning electron microscopy. The resulting micrographs (magnification of 30,000:1) are shown in Figure 12a (Example 304) and Figure 12b (Comparative Example 302).

Figure 12a shows "raspberry"-shaped composite particles resulting from the adsorption of the small latex particles on the surfaces of the larger titanium dioxide particles. By contrast, the smooth titanium dioxide particles and the unadsorbed latex particles seen in Figure 12b demonstrate the absence of such

adsorption for a conventional phosphoethyl methacrylate-free latex. These micrographs provide a direct visual confirmation of the adsorption process of the present invention.

### Example\_305

An acrylate polymeric latex emulsion was prepared having a calculated glass transition temperature of about 14°C, a particle size of 161 nm, and total solids of about 45 percent by weight using a single-stage, gradual-addition thermal process from monomer including 1.3 percent by weight methacrylic acid and one percent by weight phosphoethyl methacrylate (Latex B). A pigment grind was prepared by grinding together at high speed 200 parts by weight TiPure R-900 titanium dioxide, 8 parts by weight Tamol 731 pigment dispersant, 1 part by weight Colloid 643 defoamer, 20 parts by weight propylene glycol and 30 parts by weight water. 495.6 parts by weight of Latex B were mixed at low speed with 7.57 parts by weight water and 22.64 parts by weight Texanol. Subsequently, to the Latex B/Texanol mixture were added 9.70 parts by weight Triton X-405 surfactant, 49.57 parts by weight water, 4 parts by weight Colloid 643 defoamer, 59 parts by weight propylene glycol, and 6 parts by weight Nuosept 95 preservative. To this mixture was added the grind, and subsequently, 100.4 parts by weight of a 5.0 percent by weight solution of Natrosol 250 MR hydroxycellulose thickener were added to provide a paint (Example 305) with a PVC of 20, a calculated volume solids of 32 percent, and a calculated weight solids of 42.1 percent. The hiding and gloss of the paint were evaluated and compared with a control paint prepared from an polymeric latex made using a similar process but omitting the phosphoethyl methacrylate (Comparative Example 303), the results being given in Table CII, and showing improved hiding and gloss using the process of the present invention.

Table\_CII

_Example_	Hiding	20°Gloss	60°Gloss
Comp. 303	. . . . . 6.9	14	54
305	. . . . . 7.8	24	63

## Example 306

... This is an example of latex particles adsorbed on a latex particle. In this example, a latex with 44 EA/47MMA/9DMAPMA (dimethylaminopropylmethacrylate) composition and 960 nm particle size was used as core particle. We used 44EA/33MMA/20Sty/3AA latex with 350 nm p.s. as outer latex. The zeta potentials (measured by Malvern Zetasizer) of 0.5% latex solution in different pH (adjusted with  $\text{NH}_4\text{OH}$  or acetic anhydride) are as follows:

Latex	44EA/47MMA/9DMAPMA	Latex	44EA/33MMA/20Sty/3AA
<u>pH</u>	<u>Zeta Potential</u>	<u>pH</u>	<u>Zeta Potential</u>
3.0	60mv	2.7	-67mv
4.1	59mv	5.1	-67mv
5.4	57mv	6.7	-65mv
6.6	49mv	8.8	-62mv
6.8	45mv	11.3	-69mv
7.1	45mv		
9.4	-3.5mv		
10.3	-52mv		
11.3	-50mv		

The adsorption experiments were done by adding 4% core latex to 10% outer latex at specified pH (adjusted latex to same pH before mixing) under bench stirring. The results from optical microscope observation are:

.... pH	.... <u>Optical Microscope</u>
.... 5	.... Unstable, agglomerate
.... 7	.... adsorption with multiple core particles
.... 8	.... adsorption with multiple core particles
.... 9	.... adsorption with multiple core particles
.... 10	.... adsorption with small amounts of double, .... triplet core particles
.... 11	.... no adsorption

The results show that agglomeration occurs with core particles having positive zeta potential. It is free of visual grit and useful. The zeta potential of two particles are about -35mv and -65mv at pH 10 and the difference is about 30mv.

#### Example 307

This is an example of composite particles according to the present invention adsorbed onto the surface of a third particle, in this case an inorganic particle. Ti-Pure R-900 TiO<sub>2</sub> pigment was added to a 100 nm, Tg=3°C latex while mixing at high speed on a disc disperser to give a pigment grind with a PVC of 38% and 35% volume solids. The concentration of unadsorbed latex in the supernatant was determined gravimetrically to be very low. To this was added an aqueous suspension of Duramite (trade mark of Thompson-Weinman & Co) calcium carbonate (mean particle size 12.5 microns) until optical microscopy indicated that essentially all of the latex-titanium dioxide particles were adsorbed on the surface of the Duramite calcium carbonate particles. The composition of the final suspension of these (multi-) composite particles was 90% calcium carbonate, 4% titanium dioxide, and 6% latex by volume.



CLAIMS

1. A process for forming a suspension of discrete composite particles  
each composite particle comprising an insoluble first particle and at least one insoluble second particle on the surface of the first particle  
comprising mixing the first particles with the second particles under conditions to form a suspension substantially free of agglomerates comprising multiple first particles and agglomerates consisting of just multiple second particles;  
wherein the conditions are such that the mixture is only slightly unstable towards heteroagglomeration of the first and second particles.
2. A process according to Claim 1 wherein the first particles are the same and the second particles are the same.
3. A process according to Claim 1 or Claim 2 wherein the first particles or the second particles are inorganic particles and the other of the first particles or the second particles are organic particles.
4. A process according to Claim 3 wherein the inorganic particles are  $\text{TiO}_2$  particles.
5. A process according to Claim 4 or Claim 5 wherein the organic particles are polymer latex particles.
6. A process according to any one of the preceding claims wherein either the first particles or the second particles comprise a chemical group for attachment to the other of the first particles or the second particles.
7. A process according to Claim 6 wherein the chemical group is based on a polymerizable ethylenically unsaturated acid-functional monomer.
8. A process according to any one of the preceding Claims wherein the first and second particles have the same sign of surface charge.
9. A process according to any one of the preceding Claims wherein the surface potential of each first particle is different from the surface potential of each second particle.
10. A suspension of at least 10% solids of composite particles obtainable by a process according to any of Claims 1 to 9.

11. A discrete multi-composite particle comprising at least one composite particle as defined in any one of the preceding Claims adsorbed on the surface of a third particle.

1/13

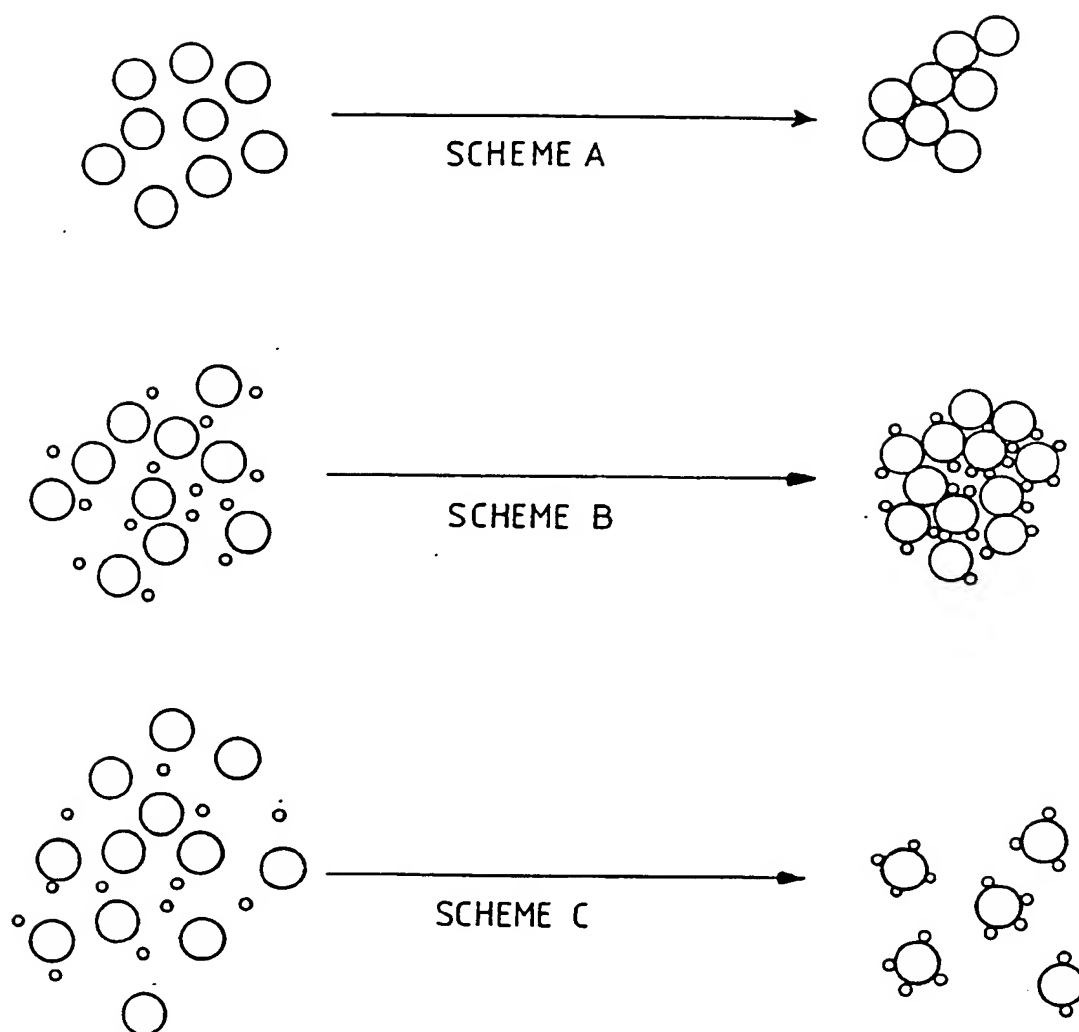


FIG.1a.

**SUBSTITUTE SHEET**

2/13

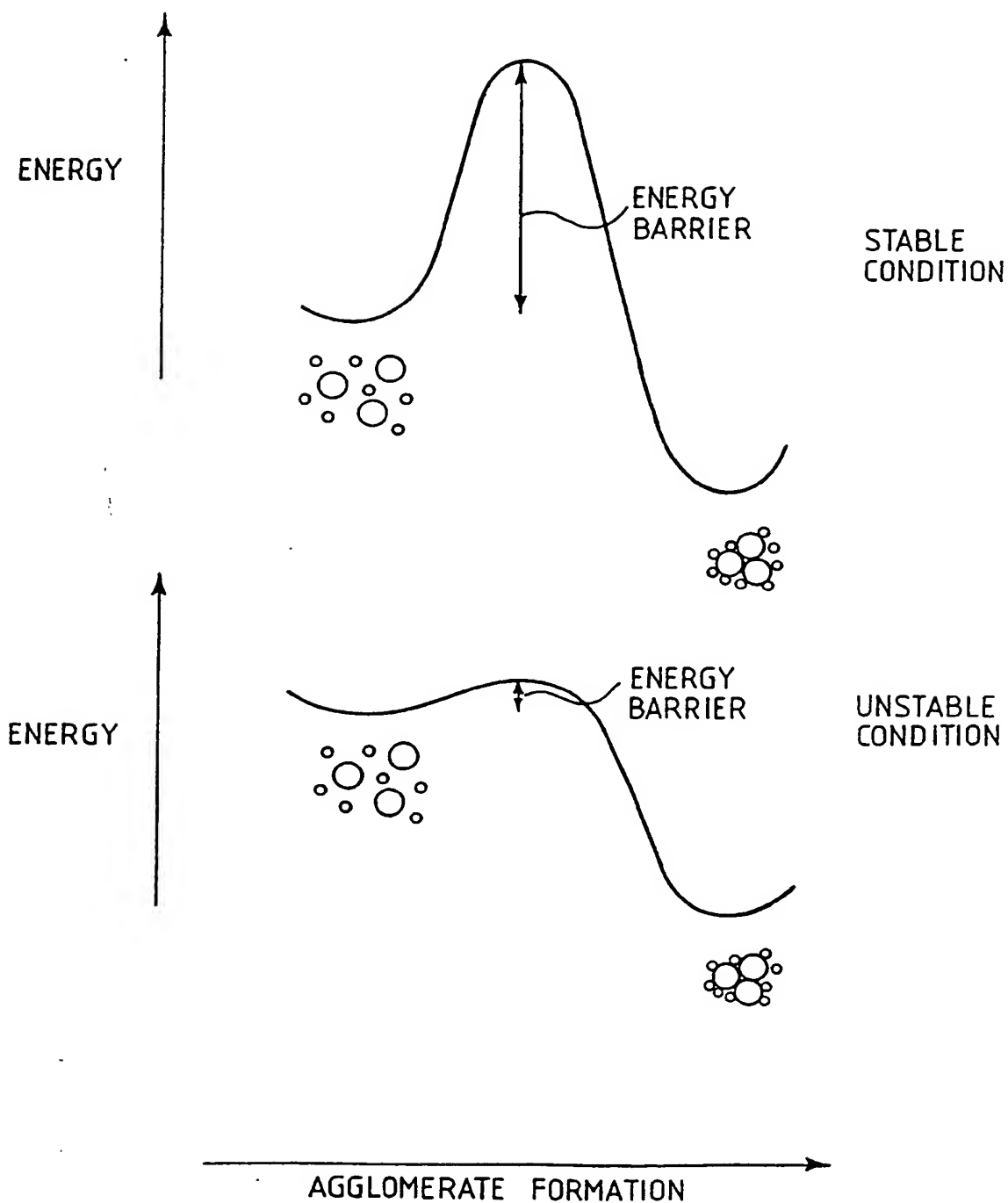


FIG.1b.

**SUBSTITUTE SHEET**

3/13

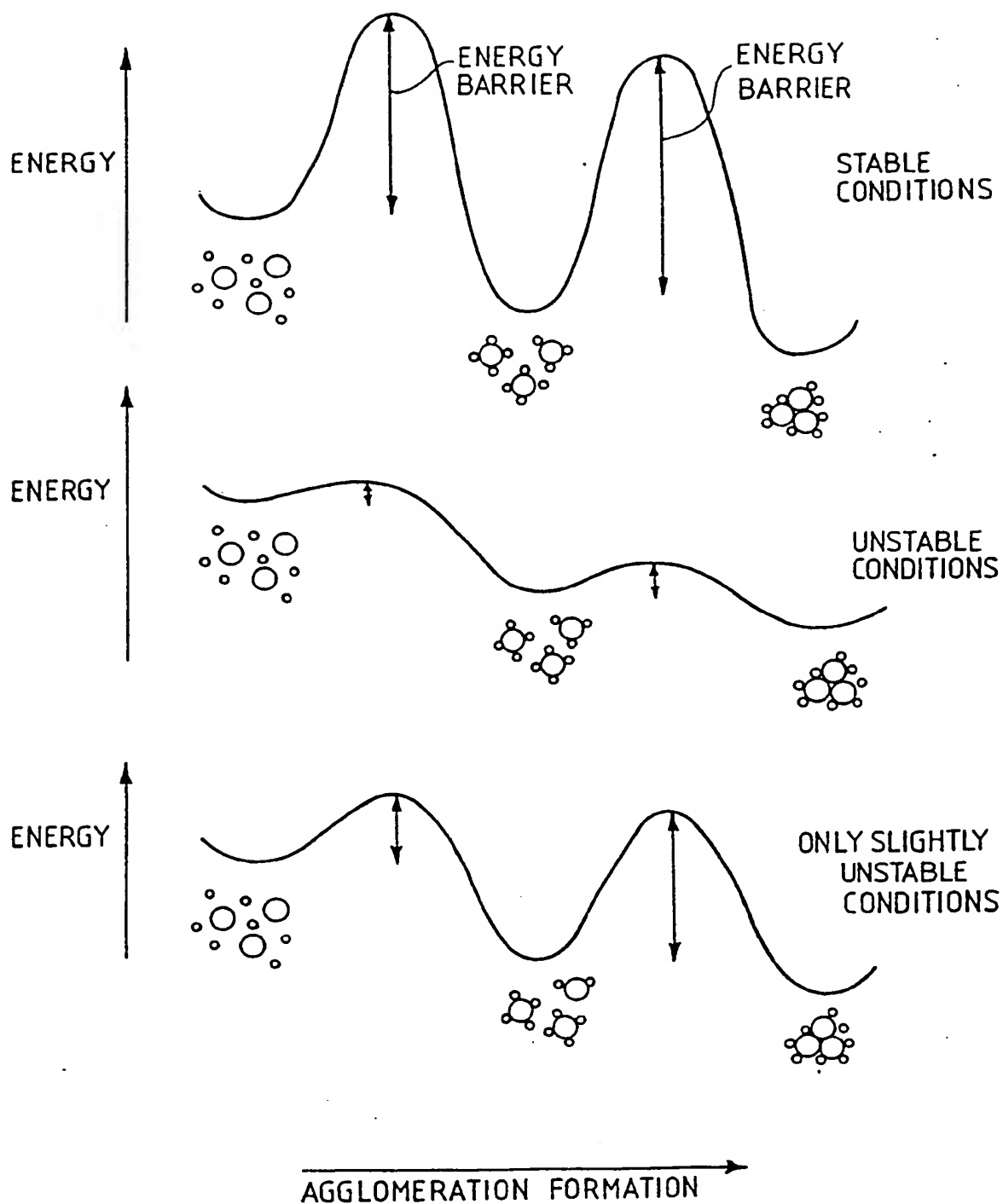


FIG.1c.

SUBSTITUTE SHEET

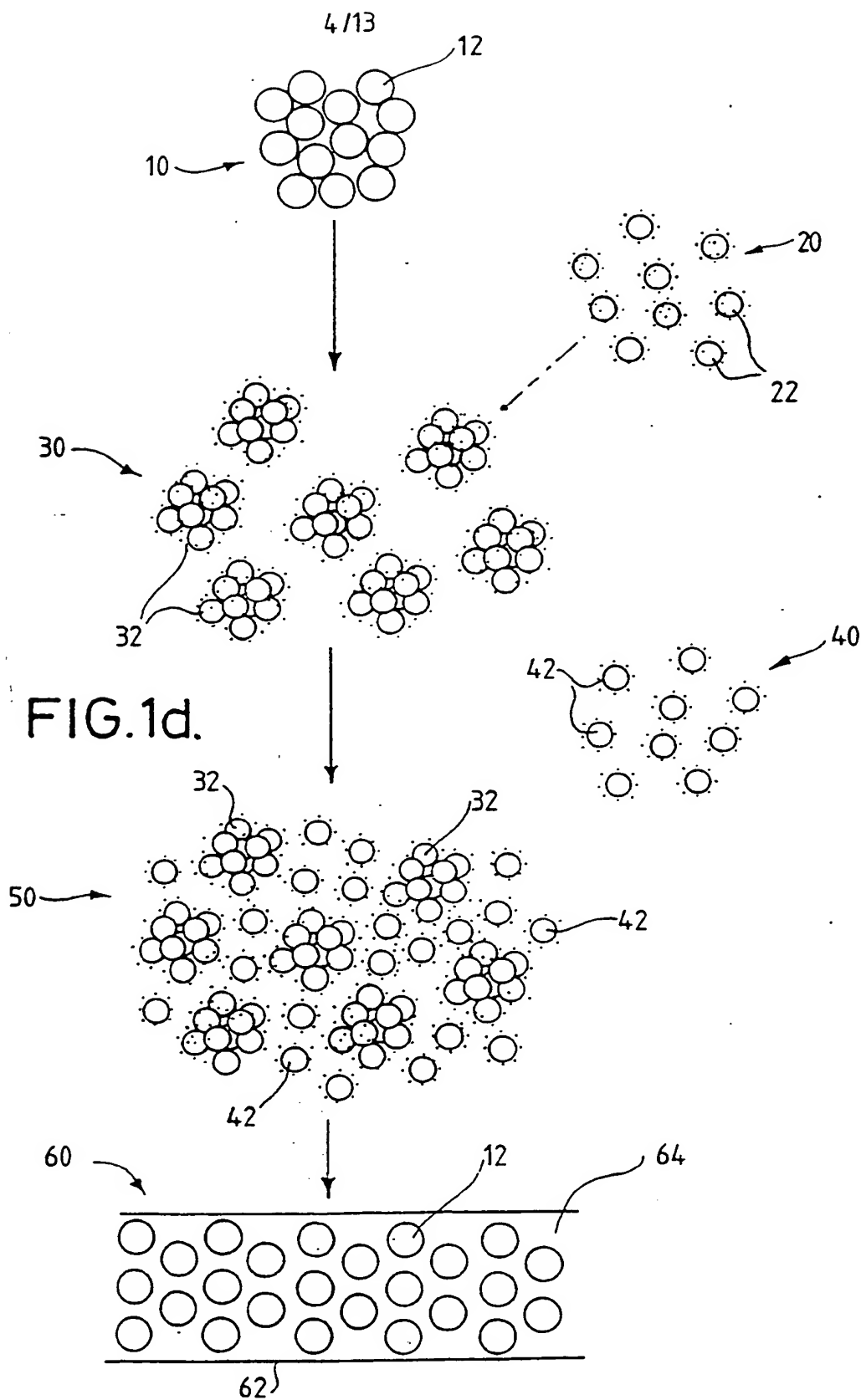


FIG.1d.

**SUBSTITUTE SHEET**

5/13

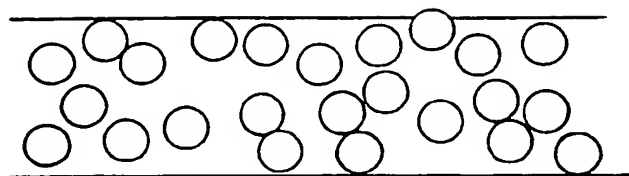


FIG.2.

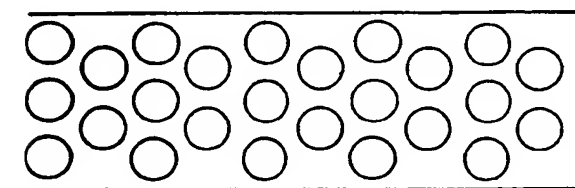


FIG.3.

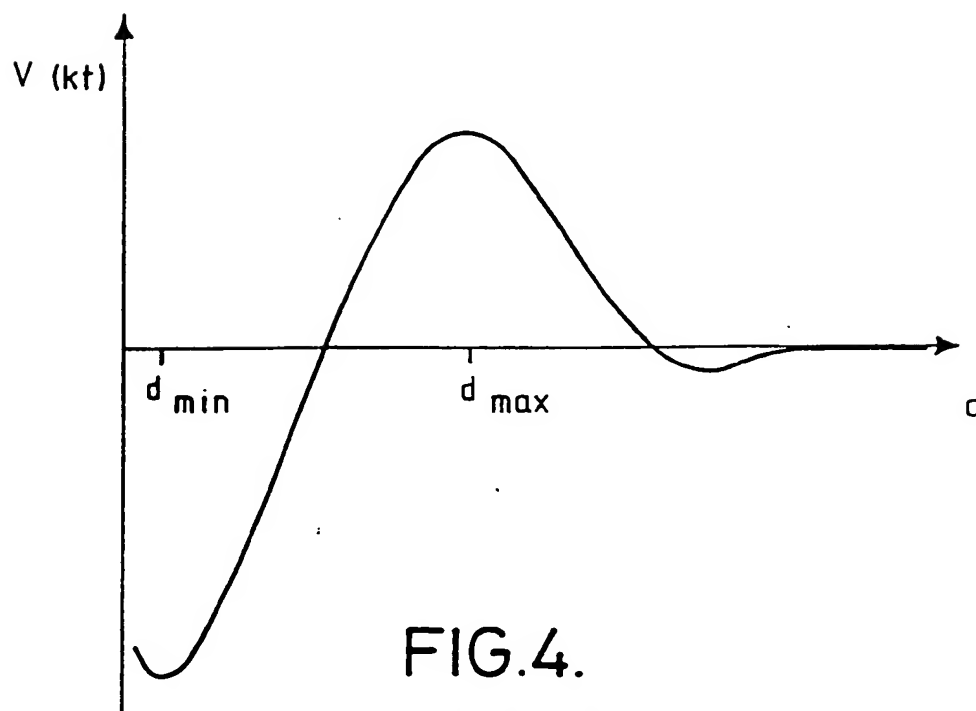


FIG.4.

**SUBSTITUTE SHEET**

6/13

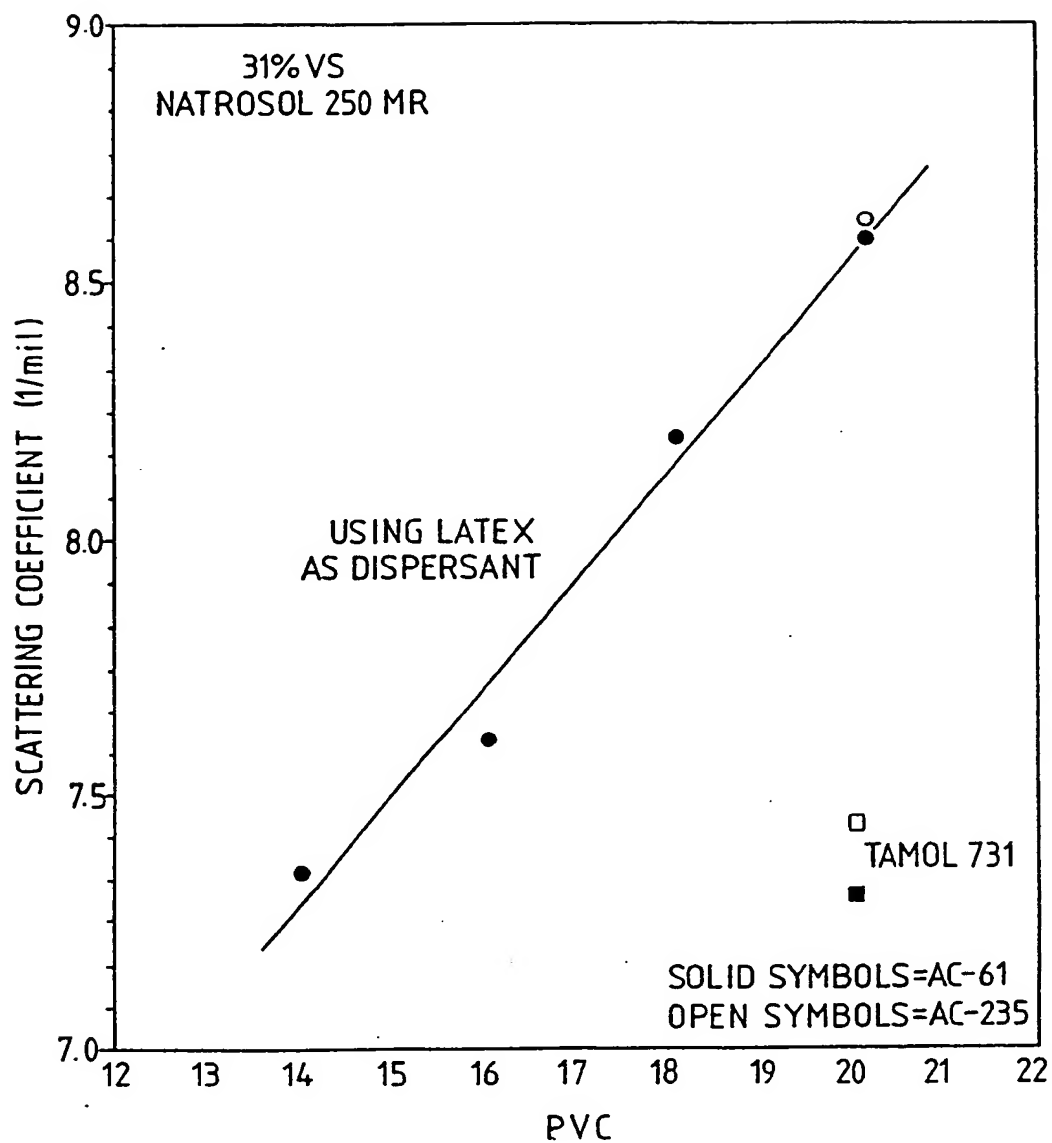


FIG.5.

SUBSTITUTE SHEET



7/13

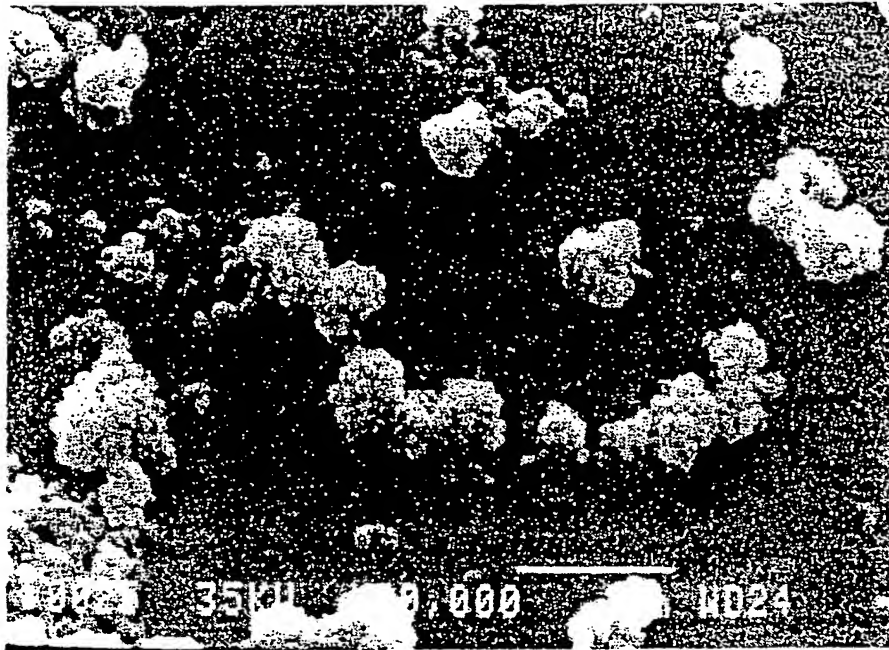


FIG.6a.

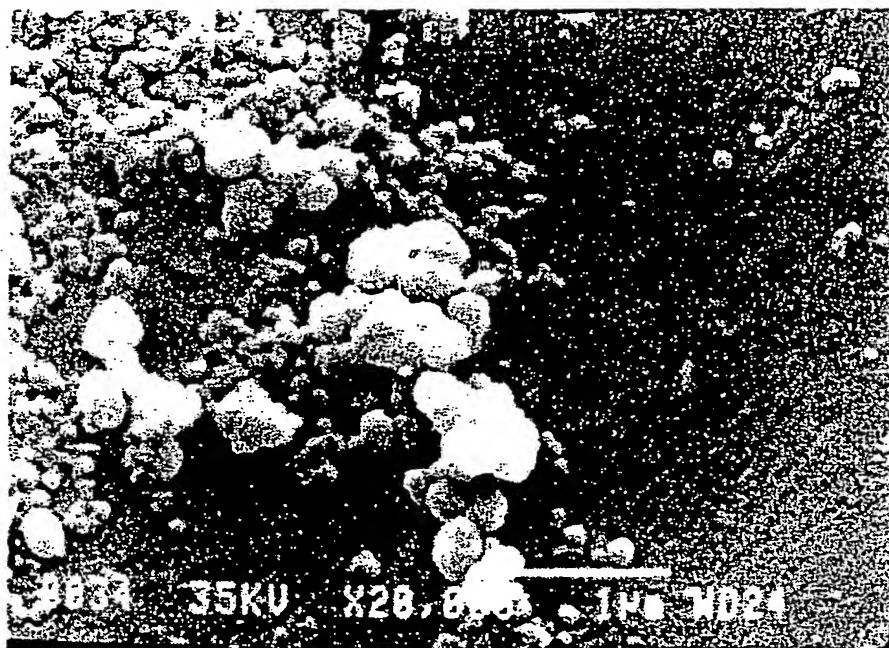


FIG.6b.

SUBSTITUTE SHEET

8/13



FIG. 7.

SUBSTITUTE SHEET

9/13

FIG.8a.

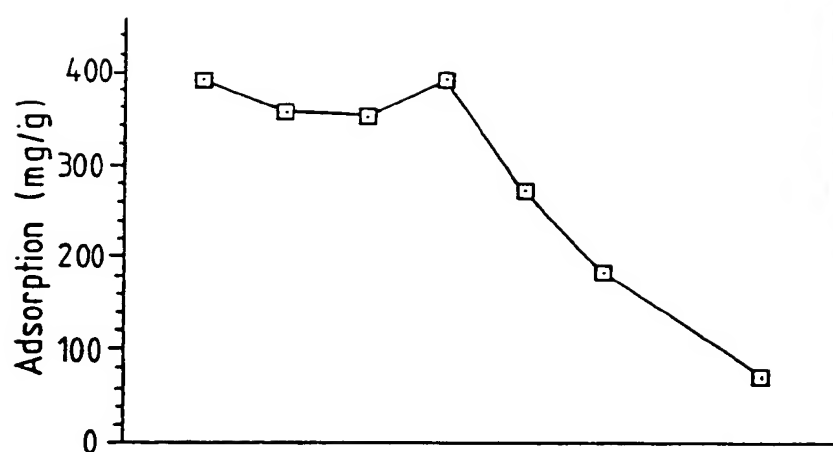


FIG.8b.

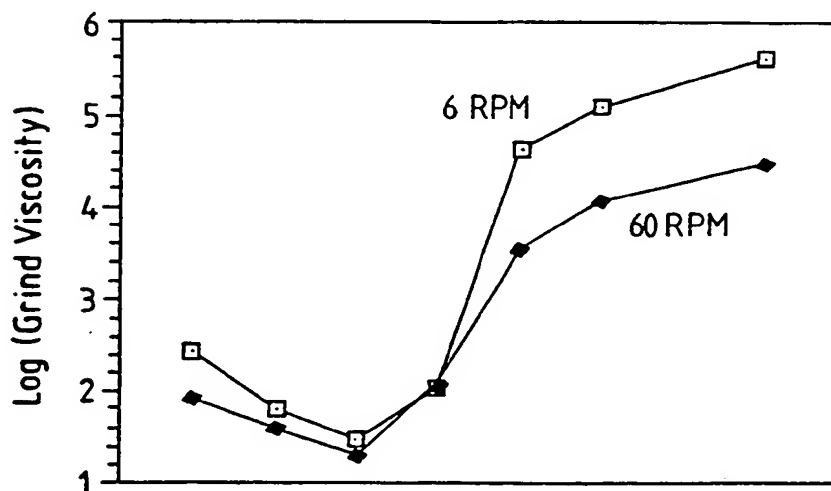
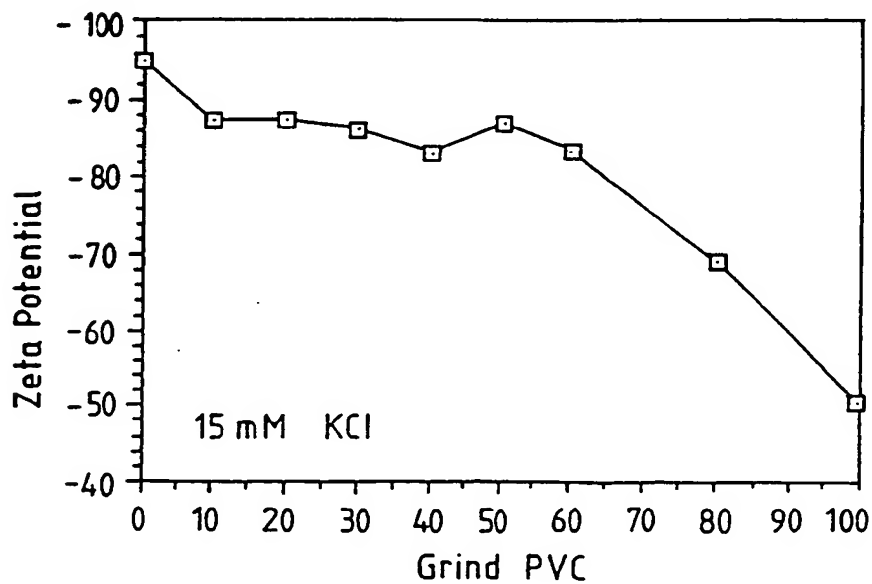


FIG.8c.



SUBSTITUTE SHEET

10/13

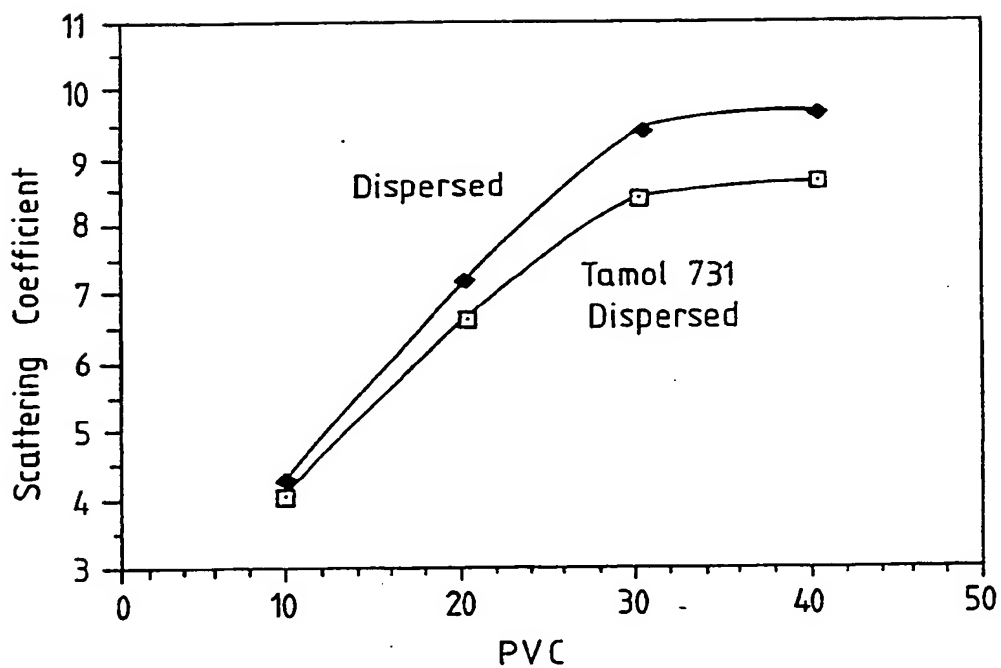


FIG.9.

SUBSTITUTE SHEET

11/13

FIG.10a.

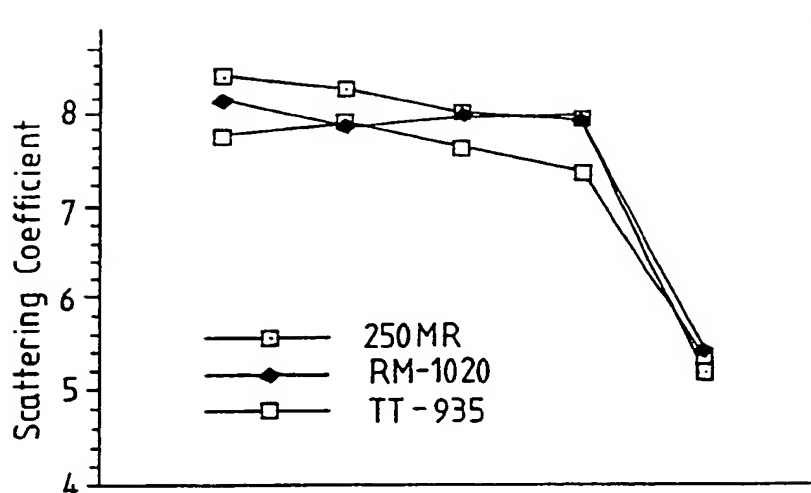


FIG.10b.

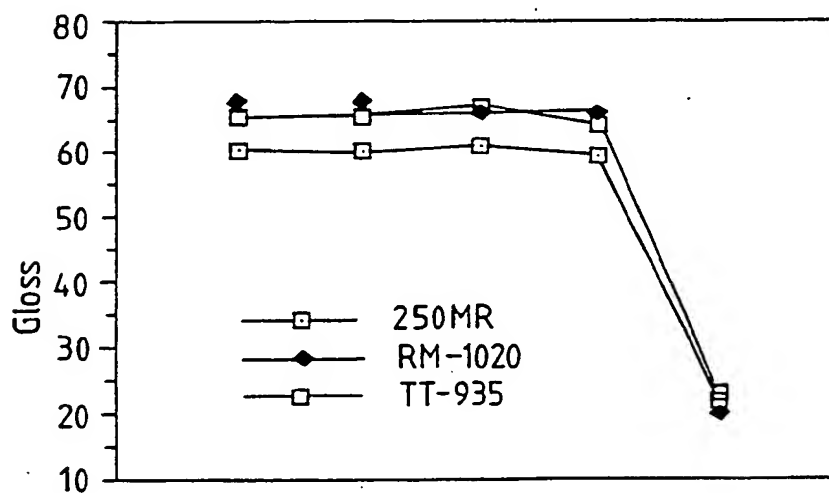
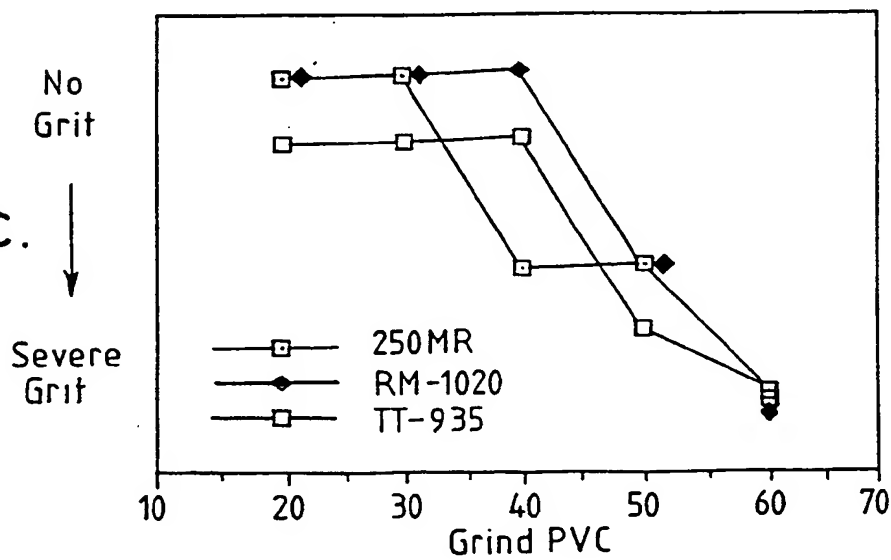
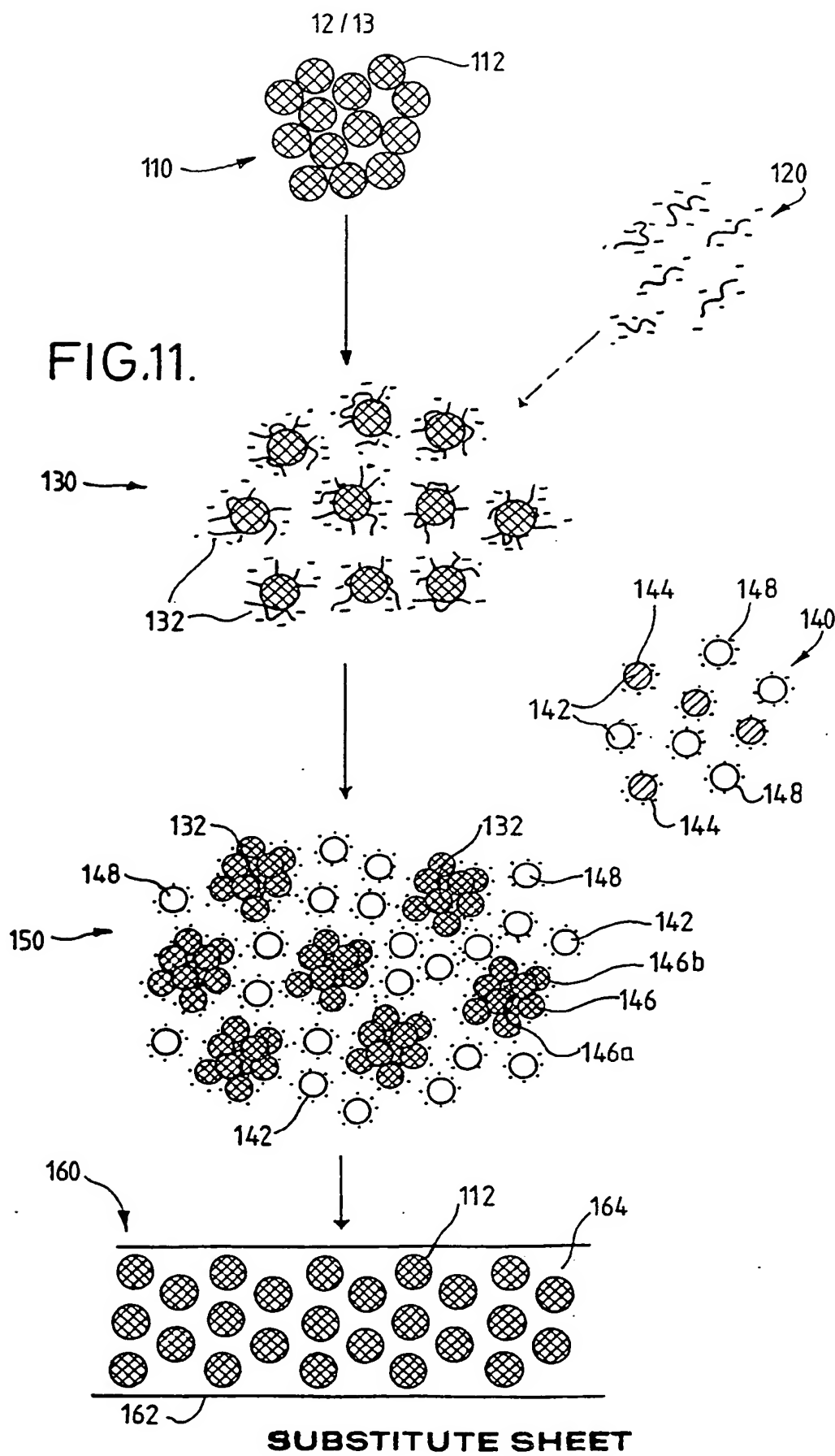


FIG.10c.



SUBSTITUTE SHEET



13/13

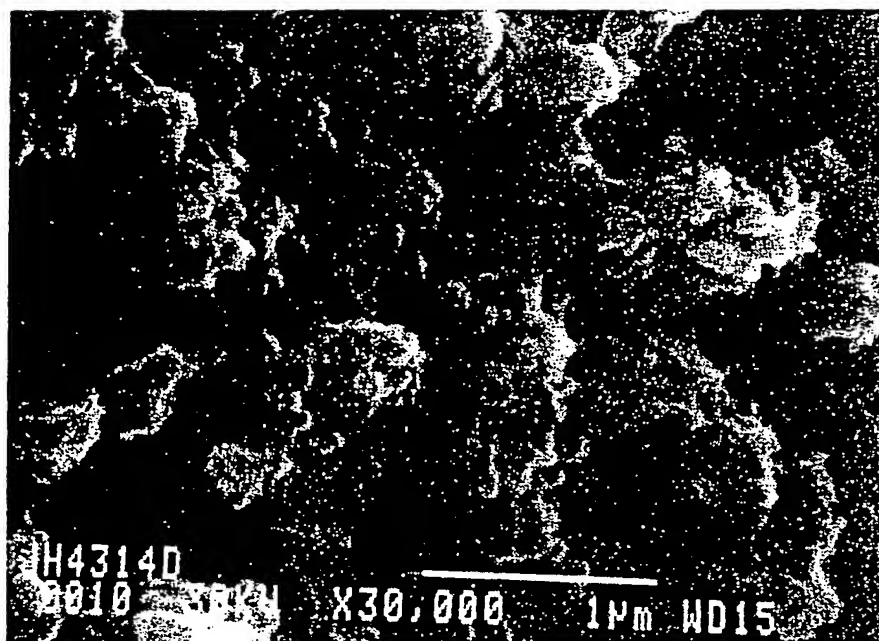


FIG.12a.

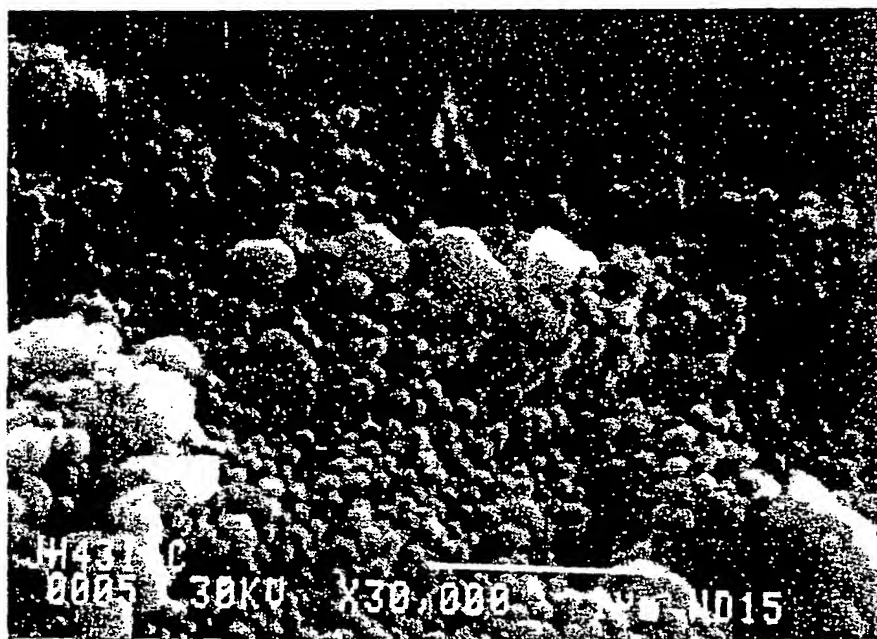


FIG.12b.

SUBSTITUTE SHEET

## INTERNATIONAL SEARCH REPORT

PCT/US 92/09731

International Application No

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C09D5/02; C09D7/12; C09D7/00; C09C1/00		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C09D ; C09C	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	US,A,1 766 592 (J. BLUMENFELD) 24 June 1930 see left column, line 1 - line 10 see left column, line 44 - line 49 ---	1,4,10
X	GB,A,2 220 666 (ECC INTERNATIONAL) 17 January 1990 see claims 1,10-12 ---	1,3-5, 10,11
X	US,A,4 025 483 (A. RAMIG, JR.) 24 May 1977 cited in the application see column 1, line 45 - line 49; claims 1-6 see column 2, line 1 - line 50 ---	1,4,5,10
A	EP,A,0 337 672 (CROWN DECORATIVE PRODUCTS) 18 October 1989 ---	
-/--		
<p><sup>10</sup> Special categories of cited documents : <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
05 APRIL 1993		17.05.93
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		VAN BELLINGEN I.

Form PCT/ISA/210 (second sheet) (January 1985)



III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 421 238 (HOECHST) 10 April 1991 ---	
A	EP,A,0 113 435 (DESOTO) 18 July 1984 -----	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9209731  
SA 67885

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 05/04/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-1766592		None	
GB-A-2220666	17-01-90	US-A- 5028482 AU-B- 620115 AU-A- 3791789 EP-A- 0359362 JP-A- 2067341	02-07-91 13-02-92 18-01-90 21-03-90 07-03-90
US-A-4025483	24-05-77	None	
EP-A-0337672	18-10-89	AU-B- 615530 AU-A- 3262089 GB-A, B 2217334 JP-A- 1315473	03-10-91 19-10-89 25-10-89 20-12-89
EP-A-0421238	10-04-91	DE-A- 3932816 CA-A- 2026454 JP-A- 3124774 US-A- 5135970	11-04-91 31-03-91 28-05-91 04-08-92
EP-A-0113435	18-07-84	US-A- 4474909 US-A- 4474910 US-A- 4474911 CA-A- 1226400 JP-A- 59115367	02-10-84 02-10-84 02-10-84 01-09-87 03-07-84

EPO FORM P0079

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82